A STUDY OF STRUCTURE-PROPERTY RELATIONSHIPS IN CERTAIN POLYMERIC DENTAL MATERIALS

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DECLARATION

I hereby declare that the work presented in this thesis was carried out by me at Dundee College of Technology, Dundee, except where due acknowledgement is made, and has not been submitted by me for any other degree.

Signe[redacted].....

Date ..8/3/88.....

ABSTRACT

Acrylic resin artificial teeth may be produced by Transfer or Pseudo compression moulding. Both of these moulding techniques were investigated to formulate the best conditions for use in a mass production environment and evaluated on a commercial basis. It was found that the transfer technique, despite higher material costs, was the most commercially viable.

The effects of seven process variables on the mechanical properties of polymer systems produced by the transfer method were evaluated by comparing their stiffness, strength, viscoelastic behaviour, and hardness. The variables studied were: temperature, pressure, material condition, crosslinking agent concentration, concentration of BisGMA/THFMA, monomer: polymer ratio, and the initiator concentration. It was found that some of these variables and their interactions affected the properties of the polymer produced to varying degrees.

Using the above study as a screening technique to identify the variables which improved the performance of the polymer system, the effects of BisGMA/THFMA and benzoyl peroxide initiator were studied in greater depth. Mathematical models have been constructed which describe the effect of BisGMA/THFMA and benzoyl peroxide on the stiffness and viscoelasticity of the polymer. Consideration of these models and the effects the two variables have on the strength of the polymer produced indicated that 40% BisGMA/THFMA (by volume of liquid) and 2.16% benzoyl peroxide (by weight of mix) are the optimum levels of the variables.

The effect of reinforcing this optimum formulation with different volume fractions of 2μm silica was evaluated. Stiffness, surface hardness and viscoelastic properties increase but strength is reduced.

An organozirconate coupling agent was added to untreated silica (particle size of 50 nM). It is found that the coupling agent modifies both the rheology of the unpolymerised composite resin and the mechanical properties of the resin itself.

The synthesis of the diketone derivative of BisGMA, termed BisGMAO, was investigated. Several oxidations of BisGMA were attempted in order to achieve a high yield of BisGMAO. Polymerisation of both monomers and the evaluation of their mechanical properties of the derived polymers showed BisGMA to be superior.

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FOREWARD

Bracketed arabic numerals in the text refer to the diagrams of the formulae and the arabic superscripts indicate references. The following abbreviations have been used in the text.

BisGMA - 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane

BisGMAO - 2,2-bis-[4-(2-OXO-3-methacryloyloxypropoxylphenyl]propane

DMSO - Dimethylsulphoxide

DMTA - Dynamic Mechanical Thermal Analysis

EGDMA - Ethyleneglycol dimethacrylate

$MgSO_4$ - Magnesium Sulphate

MMA - Methyl methacrylate

PMMA - Poly(methyl methacrylate)

CONTENTS

To Mum, Dad, Fraser, and Lesley

Chapter 1: GENERAL INTRODUCTION

1.1 AIM

The aim of this research is to investigate structure-property relationships that exist in acrylic resin teeth and, thus, the effect that several process variables may have on the mechanical properties of the teeth. Knowledge of the effects of specific manufacturing process variables on the polymer structure, and hence on the mechanical properties, enables the formulation of a resin which improves the mechanical performance of the acrylic teeth.

An obvious extension was to introduce different volume fractions of fine particle silica, coated with organosilane, to the optimum resin formulation determined above. The effect of filler volume fraction on the mechanical properties of a high temperature, low time cycle, cured acrylic was ascertained. A crucial factor in determining the final properties of any composite is the interfacial bond between the resin and filler phases[1]. Consequently, the effect of using a tetravalent organozirconate as a coupling agent between the resin and filler phases was studied.

Finally, the synthesis of a novel monomer based on BisGMA was attempted. The aim was to prepare a monomer which had all the advantages of BisGMA including reduced polymerisation shrinkage and increased strength and stiffness. However, the material should not have the disadvantages associated with BisGMA, such as low purity and high viscosity.

Armed with a knowledge of the effects that several process conditions, filler volume fraction, coupling agents, and a novel monomer have on the mechanical properties of the artificial

resin teeth it was anticipated that a material could be formulated which had superior mechanical properties, and would thus be more clinically acceptable.

The following chapter describes the concepts involved in the mass production of artificial acrylic resin teeth and the techniques employed for the evaluation of their mechanical performance. This will involve a discussion of the history of artificial teeth, the different manufacturing techniques available for moulding artificial teeth, and a description of the mechanical tests and the information that may be yielded.

1.2 THE HISTORY AND DEVELOPMENT OF ARTIFICIAL TEETH

The first civilisations to show examples of dental prosthesis were the Phoenicians and Ertuscans several hundred years BC. If the patient was wealthy the replacement teeth were human. Poorer mortals had to be satisfied with replacements carved from animal teeth, or nothing at all! The teeth were held in position with wire[2].

In 1728 Fauchard described a method for the manufacture of complete ivory dentures, while in 1775 Bourdet introduced ivory teeth attached to a gold base using gold pins[2].

Another Frenchman, de Chemant, patented a process for the manufacture of porcelain dentures in 1792[3]. The aesthetics of porcelain teeth were improved by Guiseppananelgo Fonzi[2], an Italian dentist, who prepared single porcelain teeth in twenty six different shades. Each tooth had platinum hooks so they could be attached to a plate. The different shades of porcelain were achieved by using metal oxides - a technique still used today!

The result of Fonzi's work was that by the early 1800's a dentist could prepare replacement, artificial teeth which would make partial and full dentures appear more life-like.

In 1937 an acrylic resin, PMMA, was first used as a denture base. Initially PMMA teeth were compression moulded or injection moulded 'powder' teeth. They were called powder teeth because they were processed using only PMMA powder. These teeth were not satisfactory because they often crazed or disintegrated in use. Another problem associated with the acrylic teeth was that of blushing, ie there was a colour change during processing of the denture. The degree of severity of these problems was reduced when the process for production of the acrylic teeth was changed from the powder technique to the powder/liquid acrylic dough technique[4]. Such powder/liquid doughs were being used to produce denture base so it was a logical extension to introduce the technique for artificial teeth. The powder contained excess initiator which polymerised the liquid monomer when the dough was heated above 55°C. The resulting solid was a heterogeneous material made up of the polymerised monomer with the solid PMMA[5].

Crazing in acrylic teeth was overcome by the addition of a crosslinking agent, such as EGDMA[6]. In 1952, Dirksen[7] identified the advantages, disadvantages and limitations of plastic artificial teeth. He noted that artificial teeth had several advantages. They were easily ground and polished; they had a natural appearance and feel; they were tough and had high resilience; were non-toxic; insoluble in oral fluids, and bonded well to denture base without the need for mechanical

retention. Disadvantages included their softness and low abrasion resistance; dimensional change on absorbance of oral fluids; low heat distortion temperature; cold flow or permanent deformation below their elastic limit; and crazing and blanching. The last was improved by introduction of a crosslinking agent, but this reduced the propensity of the tooth to bond to the denture base[2]. To overcome this drawback, teeth were developed in which the labial component of the tooth was crosslinked to a degree which resisted crazing whilst the lingual portion was more lightly crosslinked, affording a better bond between the base and the tooth[8].

As they have a low heat distortion temperature care must be taken during the construction of waxed dentures containing acrylic teeth. If the flame from the burner used to warm and melt the wax is sufficient to raise the temperature of the teeth above their glass transition temperature, they will deform. Several acrylic tooth manufacturers have added speciality acrylic monomers to their formulations[9] which may increase the mechanical properties of the tooth. The hardness and abrasion resistance of acrylic teeth has been claimed to be improved by the addition of fine inorganic fillers to the labial portion of the tooth[10]. Use of coupling agents such as γ-methacryloxypropoxysilane gives a good bond between the filler and the acrylic if the filler is silanated under optimum conditions[11]. The lingual portion may be, either partially filled, or unfilled, thus affording a good bond between the denture base and the tooth. Poor abrasion resistance is regarded as a disadvantage because if the teeth

wear away the bite of the denture will be diminished[2].

The resistance of the acrylic tooth to deformation from an applied stress has also been increased by incorporation of fillers[4]. Other claimed methods include the use of speciality monomers[12] and the formation of interpenetrating networks[13]. Such interpenetrating networks are prepared by crosslinking a monomer in the presence of a swollen crosslinked polymer[14].

The addition of crosslinking agents, speciality acrylic resins such as BisGMA, and fine particle size inorganic fillers have improved the performance of acrylic resin teeth. However, they still do not match the mechanical properties of natural teeth with regard to hardness, abrasion resistance, modulus and dimensional stability.

Due to the phenomenon of creep, the acrylic resin teeth eventually lose the characterisation marks which are added to improve their aesthetic qualities. It is important that the teeth retain the characterisation marks which were designed to improve the realistic appearance of the tooth and give the patient confidence. Similarly, the degree of translucency, shade, and propensity of the tooth to fluoresce, must match the natural teeth of the patient in the case of partial dentures, or match the colouring of the patient in the case of full dentures.

Several different designs of acrylic teeth have been introduced to improve the aesthetics of the tooth. Monochrome teeth, which are the most basic design, have only one shade and are one-piece teeth. In an attempt to improve the aesthetic quality of these teeth, an incisal or labial layer is moulded onto the body of the tooth. This layer is only very lightly

pigmented in an attempt to create a translucent surface on the tooth. The lingual part of the tooth is then moulded onto the labial surface. The lingual component is more heavily pigmented to create the correct shade of tooth. Such teeth are called polychrome teeth. Some companies are reported to build up four or five layers of colour.[15] These teeth have moulded-in stains in an attempt to make the teeth more realistic. The exact number of layers is however usually a guarded secret.

To ensure that the acrylic resin artificial teeth will conform to a minimum level of clinical performance, bodies such as the British Standards Institute[16], the American Dental Association[17] and the International Standards Organisation[18] have all specified levels of mechanical and aesthetic behaviour they feel will identify clinically acceptable teeth. A copy of the British Standard 3990 (1980) is in Appendix 3. With regards to aesthetic performance, the teeth must match both the shade and dimensions stated by the manufacture in the shade guide. The teeth must retain their shade after processing and must not blush or distort. Similarly they must keep their colour after being subjected to UV light for 24 hours whilst being submerged in water. The teeth must also be able to regain their surface finish on polishing after being processed. The teeth must also not have any visible porosity when inspected under X10 magnification.

Mechanically, the teeth must pass an environmental stress crazing test in which the teeth before and after processing are immersed in MMA. Crazes show up as apparent cracks. The crazing test is clinically valid because during the preparation

or repair of a denture the acrylic resin teeth may come in contact with MMA.

A bonding test is specified to ensure that an adequate bond is created between a tooth and the denture base. If the tooth is pulled cleanly from the denture then there is insufficient bonding. Clearly this test is of great clinical significance as it may prove fatal if a tooth was to fall from a denture base. At the very least a tooth coming off from a denture base would cause extra expense for a dentist or a laboratory because of repair costs. This in turn would afford a reduction in product confidence in the tooth which may spell disaster for a tooth manufacturer. Finally, the hardness of the tooth must be above a specified value. The significance of the hardness test is discussed in greater depth later, (see Section 1.4.3).

1.3 MANUFACTURING PROCESSES FOR THE PRODUCTION OF ACRYLIC TEETH

Transfer, compression and pseudo-compression moulding are the three most commonly employed moulding methods for the manufacture of acrylic teeth. The relative merits/demerits of each system will be discussed below.

1.3.1 TRANSFER MOULDING

Transfer moulding was first employed in 1926 by the Shaw Insulator company of New Jersey. It was used to overcome the difficulty that compression moulding had in forming articles with intricate sections. It was also found to be an advantageous method when the moulded parts were complicated and where the tolerance was very close in three dimensions[19].

Transfer moulding requires the transfer of a moulding compound from a reservoir through runners or sprews into a closed heated cavity (Figure 1).

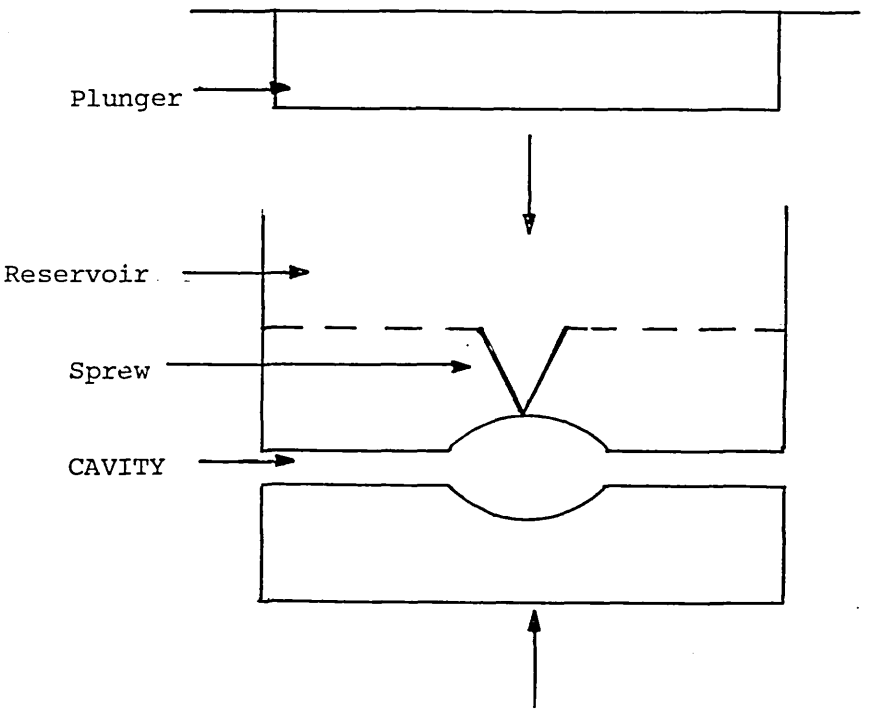


Figure 1 Example of a Transfer Mould

In the case of artificial teeth production, the mould is heated for two reasons. Firstly, the dough temperature must be raised to completely polymerise the monomer, and secondly, a higher temperature is necessary to increase the flow properties of the material to facilitate the filling of the cavity within the given time cycle.

An advantage of the transfer moulding system is that the material is being forced into the cavity. Therefore, if there is any shrinkage in the moulding the resulting pressure drop

will cause material to flow from the reservoir into the cavity. Thus, the technique will compensate for any shrinkage and, in doing so, reduce the potential reject rate.

The major disadvantage of transfer moulding is the material cost[19]. The material left in the reservoir and in the sprews is waste material. As the teeth are small articles, the percentage "scrap" in a conventional transfer mould may be as much as 80% of the material usage.

Transfer moulding may be used to manufacture mono or multi layer teeth. However, for multi layer teeth the incisal layer is usually manufactured by the compression mould technique.

1.3.2 COMPRESSION MOULDING

The earliest use of compression moulding in the polymer industry was in the early 19th century when Hancock optimised it as a technique for moulding rubber.[19] A compression mould (Figure 2) consists of two parts, a female part and a male part. When these two pieces are brought together the male part fits inside the female leaving the shape of the cavity. The two parts of the mould are brought together under pressure.

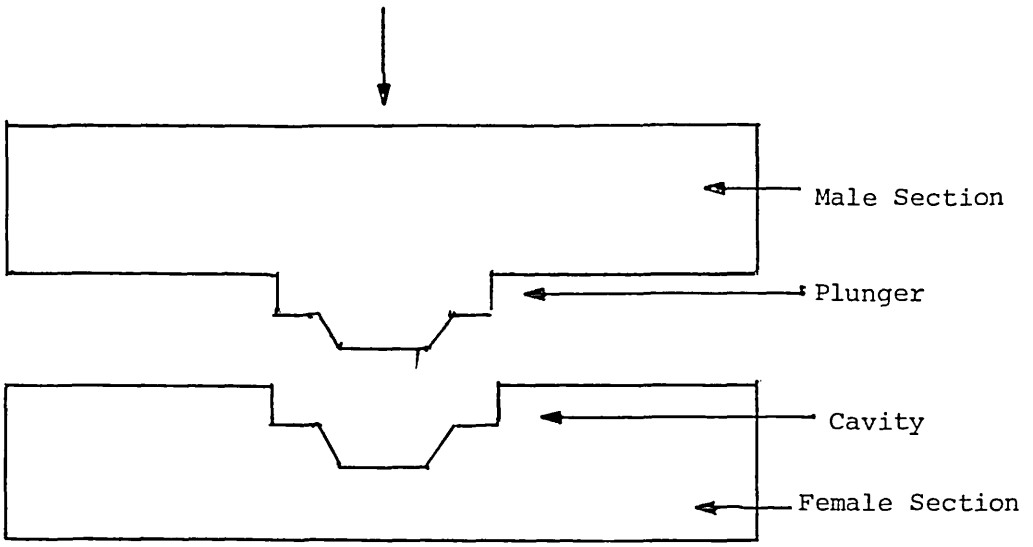


Figure 2 A Compression Mould

A pre-determined quantity of moulding compound is placed in the female part of the mould. The mould is closed and the material is cured by the action of heat.

A disadvantage of compression moulding is that to allow the escape of gases, the mould must "breathe", ie just before the mould is fully closed it is momentarily opened to allow the gases to escape, then it is closed again. If these gases do not escape this may give a porous moulding[19]. With transfer moulding it is not necessary to "breathe" the mould. To reduce the incidence of porosity in compression moulded teeth, these teeth are moulded in layers - often as many as three or four layers. This increases the time cycle for production and so increases costs. A great advantage of the compression system over the transfer method is that it produces much less

waste polymer.

Another advantage of compression moulding over transfer moulding is cost of the moulds. The compression mould, being less complex and only two part, is cheaper. Male/female type compression moulds are used in the manufacture of multi-layer teeth.

1.3.3 PSEUDO-COMPRESSION MOULDING

A pseudo-compression mould is similar to a compression mould except it consists of two female parts (Figure 3).

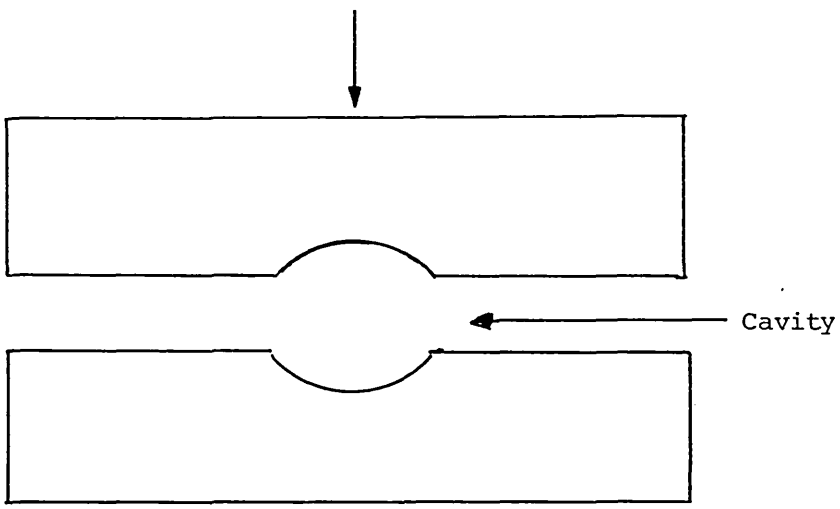


Figure 3 A Pseudo-Compression Mould

An excess of material is placed into one half of the cavity and the mould is then closed. The pressure inside the cavity is generated by the force of the ram acting on the excess of material. If there is no excess of material the force will be applied on the cavity edges. Thus, unlike transfer and compression moulding, there is no direct pressure introduced into the mould, so this process is more prone to producing defects due to shrinkage in the form of porosity and/or dull sink marks.

As there will be less pressure in the cavity in this moulding system there will be little contribution to the elevation of the boiling point of the monomer. The boiling point of a liquid is at that temperature where the vapour pressure of the liquid equals the ambient pressure [20]. Thus, to eliminate any boiling of the monomer, the temperature must be strictly controlled below the boiling point of MMA (100.3°C). The need for strict temperature control would result in an increased time cycle or reduced mechanical properties (see Chapter 3). The pseudo-compression moulding technique is exclusively used for the production of single layer teeth. Although it has the disadvantages mentioned above its great advantage is its low material usage and waste polymer generated.

1.3.4 IMPORTANCE OF RHEOLOGY DURING MOULDING

It is imperative, irrespective of the moulding system used, that during moulding the material completely fills the cavity. A material will only do so if it has the appropriate flow properties during the moulding cycle. These flow properties will be dependent on: the monomer/polymer ratio in the dough; the time the monomer and polymer are allowed to interact before moulding; the moulding pressure; the moulding temperature; and the time cycle. Thus, these independent variables must be varied to yield the optimum value of the dependent variable - the flow property of the dough material.

If the flow of the dough is too high the material will leak from the cavity via the flash lines. This leaking of material may give thick flash but good mouldings. However, the thick flash will cause problems in 'finishing' the teeth.

The thicker flash will take longer to remove, thus increasing process time and therefore, unit costs. If the flashing is more severe this will result in a pressure drop in the cavity which the reservoir of material cannot compensate for. In such cases the mouldings may contain either porosity on their surface or sink marks. In the most severe cases so much material escapes from the mould that there is insufficient left in the mould to fill the cavity and so underpacking of the mould occurs.

If the material has insufficient flow at the given moulding conditions then the flash will be reduced and, in some cases, there will be no flash. This will create problems in handling later in the finishing process when the teeth are sorted into sets. The increased handling time during sorting will increase costs.

If the flow properties are reduced further there will be insufficient flow in the material to allow for the compensation of shrinkage as the material will not readily flow into the cavity. In such cases the teeth will have sink marks and/or porosity.

Finally, the rheological properties of the material may be such that it flows so little that the mould does not fully fill.

It is, therefore, clear that if a moulding system is to be efficient and effective the moulder must have a knowledge of the rheological behaviour of the material under the moulding conditions, and the effect altering the dough formulation and condition has on its rheological properties.

1.4 EVALUATION OF POLYMERIC TOOTH MATERIALS

Fundamentally, polymeric materials are selected for a particular product because they possess the required mechanical and aesthetic properties and are economically favourable in cost.

The mechanical and aesthetic properties are dependent on the structure of the polymer - not only the chemical structure with regards to functionality, but also the polymer network. There are a large number of structural factors which influence the nature of the mechanical behaviour of polymers, examples of which are[21]:

(i) Chemical composition (eg polarity and size of functional groups).

(ii) Molecular weight.

(iii) Tacticity (eg atactic, syndiotactic, isotactic).

(iv) Type of copolymerisation (eg block, graft, random).

(v) Crosslinking and branching.

(vi) Molecular orientation.

(vii) Plasticisation.

(viii) Presence of fillers.

These structural factors will contribute to the response a material will give to an applied force. The structure of the polymer will also influence its mechanical properties in any given environment[22], for example, crosslinked acrylic is less likely to undergo environmental stress crazing by solvent attack than non crosslinked acrylics. However, the former may have inferior strength. Therefore, before a material formulation can be successfully designed to fulfil a given specification, the effects of polymer structure on mechanical properties must

be known. Similarly the mechanical properties will be affected by the environment in which the material will operate. Examples of important environmental factors which determine mechanical behaviour are[21]:

(i) Temperature.

(ii) Time/frequency of loading.

(iii) Pressure.

(iv) Type of deformation.

(v) Thermal history.

(vi) Presence of solvents.

As polymers are viscoelastic, both temperature and frequency of loading have a strong influence on the observed mechanical behaviour of polymers. Thus, the structure of the polymer will determine how the polymer will respond in a given environment. Therefore, if the mechanical properties are determined these may be correlated to structural effects. Determination of the effects of formulation variables on mechanical properties, and therefore structure, will provide data which will allow the optimisation of the product formula.

The mechanical properties of polymeric dental materials are determined by traditional plastics test methods, such as modulus and flexural strength, which are a measure of the stiffness and strength of the material[23]. Testing techniques have been elaborated in order to try and simulate service conditions encountered in the oral environment. Testing is carried out at oral temperatures and prepared samples are immersed in water to simulate the effect of water uptake in service.

However, during their service life dental materials which are placed directly in the oral cavity are subjected not only to temperature changes but also varying frequencies of loading. Clearly, information pertaining to the viscoelastic response of the material at these oral conditions is imperative for a valid evaluation of the potential polymeric dental material. In this Thesis the mechanical properties and the viscoelastic behaviour of polymeric tooth formulations were evaluated by determining tensile or flexural strength, Young's modulus surface hardness and dynamic mechanical thermal analysis.

1.4.1 EFFECT OF STRUCTURE ON TENSILE STRENGTH

Previous research[24,25] has found that tensile strength of a polymer is dependent on molecular weight below a value of approximately 4×10^5. Above this value the tensile strength reaches a limiting value. Berry[26] proposed that to obtain a higher strength the polymer molecule must be sufficiently long enough to pass from the unyielded region through the yielded region back to the unyielded region. In doing so the molecule will increase the fracture surface energy and so improve the strength of the material. If the polymer chains are below a specific molecular weight their length, when uncoiled, will be insufficient to cross from an unyielded area to the yielded and back to an unyielded. In such a case that molecule will not affect the fracture surface energy. Berry[26] reported that the fracture surface energy, and thus tensile strength, (assuming the same inherent flaw size), is dependent on molecular weight below 4×10^5. Above this value strength is independent of molecular weight as it is merely increasing the length of the

molecules in the unyielded region. In a study of the dependence of fracture surface energy on temperature and molecular structure, Berry[27] concluded that increased crosslinking reduced the strength of PMMA by reducing the surface energy by a factor of five and decreasing the inherent flaw size by a factor of three. This phenomenon was rationalised by proposing that in the crosslinked system there are less viscous or plastic processes occurring at the defect tip due to an increase in elastic behaviour and a reduction of viscous behaviour. Thus, there was less energy dissipation processes occurring.

1.4.2 EFFECT OF STRUCTURE ON THE RIGIDITY OF THE POLYMER

The modulus, or rigidity, of a polymer is dependent on the structure of the polymer network. As with strength, changes in molecular weight above a threshold value do not significantly alter the modulus[21]. The threshold value is that which is required to induce entanglements between the polymer chains.

The modulus is also increased by addition of chain stiffening groups, such as aromatic rings, to the polymer backbone. Increased crosslinking increases the modulus of a polymer by reducing the deformability of the network[21]. On the other hand, plasticisers reduce the rigidity of the network by increasing the free volume in the system, thus increasing the deformability of the system[21].

1.4.3 THE EFFECT OF STRUCTURE ON SURFACE HARDNESS

In dental materials the surface hardness of a composite or resin has been correlated to degree of cure[28]. The greater degree of conversion of the methacrylic double bonds, the harder the resin. Previous workers[29] observed that the surface layer of composites was softer due to it being rich in resin.

Thus, the surface hardness in a composite is not purely a function of the degree of cure in the resin, but also the concentration and type of filler [30]. Ruyter[31] observed that oxygen may inhibit polymerisation and this results in reduced hardness. Thus, the surface hardness is a property which, it is reported[28], can detect differences in the degree of cure in a resin. As the degree of cure may be related to molecular weight, it is not surprising that hardness may be roughly correlated to modulus[21].

1.4.4 THE EFFECT OF STRUCTURE ON THE VISCOELASTIC BEHAVIOUR OF A POLYMER

The viscoelastic behaviour of a polymer may be determined in a number of ways: dynamic mechanical analysis, dielectrics and nuclear magnetic resonance have all been employed[32]. In this study the viscoelastic behaviour of different polymer systems was measured by dynamic mechanical thermal analysis. It is appropriate at this point to give an explanation of viscoelasticity, how the viscoelastic behaviour of a polymer is determined by dynamic mechanical thermal analysis, and how this information provides information pertaining to the structure of the polymer being analysed.

(a) Viscoelasticity

The rheological properties of a theoretically ideal material can be classified as either elastic or viscous. The behaviour of real materials is relatively complex and may be described by a combination of these classifications. When a mechanical stress is imposed upon an elastic material there is an instantaneous and corresponding strain. When the stress is removed the strain also becomes zero and

the deformation is returned to the forcing body. Viscous flow, on the other hand, is not recoverable. When the stress is removed the strain remains. Hence, the work is not returned to the forcing body, but dissipated, for example, as heat or sound. Polymers are viscoelastic; ie they possess both viscous and elastic flow. The proportion of each component is characteristic of the polymer system and depends on many factors such as temperature, degree of crosslinking, molecular weight distribution, molecular structure, plasticiser content, filler type and content, and copolymerisation.

(b) Mathematical Model of Viscoelasticity

Viscoelasticity has been modelled[33] by two assemblies - the Maxwell and Voigt elements. These consist of Hookean springs and Newtonian dashpots, either in series or parallel. Such simple models adequate to describe simple viscoelastic behaviour of polymers, provide a differential equation to describe the viscoelastic time dependent behaviour of polymers.

$$a_0\sigma + a_1\frac{\partial \sigma}{dt} + a_2\frac{\partial^2\sigma}{dt^2} \ldots a_m\frac{\partial^m\sigma}{dt^m} = b\varepsilon + b_1\frac{\partial\varepsilon}{dt} + b_2\frac{\partial^2\varepsilon}{dt^2} \ldots b_n\frac{\partial^n\varepsilon}{dt^n} \quad (1)$$

where, $a_0 \ldots a_m$ and $b_0 \ldots b_n$ are material coefficients, σ = stress, ε = strain and t = time. The great advantage of this equation is that for ramp, step and sinusoidal excitations it reduces to simple forms. It is because of this simplification that straightforward links exist between the responses of creep, stress relaxation and dynamic mechanical behaviour[33,34].

(c) Dynamic Mechanical Properties of Polymeric Dental Materials

Dynamic mechanical analysis of polymeric dental materials has provided information on their viscoelastic properties[34,36]. Dynamic mechanical thermal analysis (DMTA) is a non-destructive test method which has been utilised by others using a Torsional pendulum[35,36]. This technique[32] is a resonance vibration technique, where the operator cannot control the frequency of oscillation. In addition, the technique also requires considerable expertise on the part of the operator if accurate measurements are to be obtained. However, in a forced vibration, non-resonance DMTA instrument, the frequency of oscillation can be accurately maintained. The advent of microprocessor control allows the instrument to record a large number of measurements at very small temperature intervals at a fixed frequency, thus affording much more accurate results. Since the vibrations are forced, different frequencies may be fixed. Non-resonance DMTA is carried out by impressing a small oscillatory mechanical strain on a solid and resolving the stress into real and imaginary components. In doing so, the instrument detects virtually all changes in molecular motion as temperature is scanned at a fixed frequency. DMTA is therefore a powerful tool for analysing both the molecular structure and phase morphology of a given polymeric dental material. The data obtained can be used to elucidate the effects of these factors on the physical properties of the material, such as the propensity to creep, modulus, etc. The fact that this

information is derived at low frequencies and at a range of temperatures consistent with those encountered in the oral environment means that results have greater clinical significance.

(d) Theoretical Basis of the Measurements

In a perfectly elastic solid the strain response to a sinusoidal stress is exactly in phase with the stress. The dynamic Young's modulus, (E*), is given by dividing the stress amplitude (σ_0) by the strain amplitude (ε_0) (Figure 4).

$$E^* = \frac{\sigma_0}{\varepsilon_0} \qquad (2)$$

If internal molecular motion occurs in the same frequency range as the applied strain, the material responds in a viscoelastic manner and the stress and strain are out of phase (Figure 4).

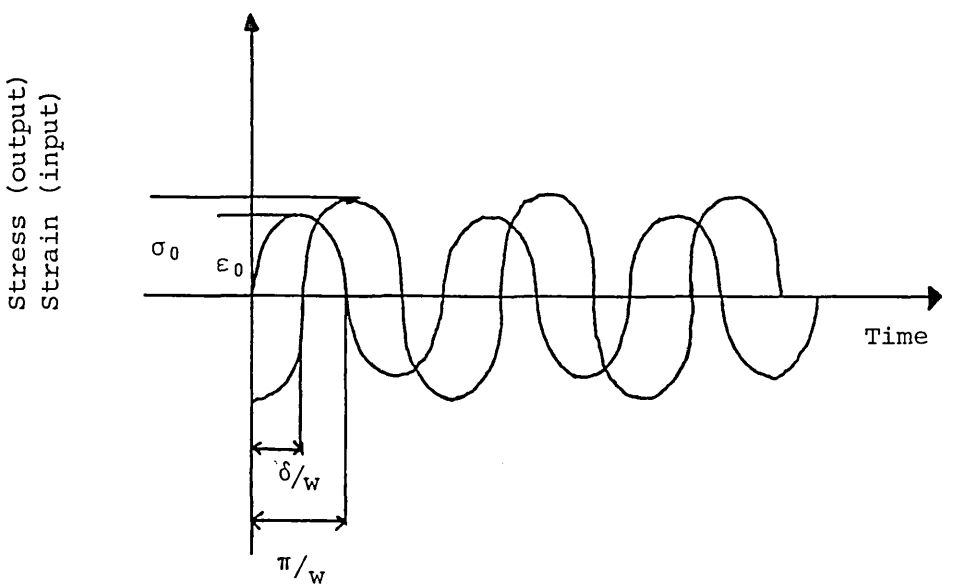


Figure 4 Strain v's Stress Response When Internal Motion Occurs

Angular frequency w = $2\pi f$ radians per second

δ = phase lag

The in-phase component of the dynamic modulus is the elastic component, and the out of-phase the viscous component.

The time lag between the two components results from the time required for molecular rearrangement and is associated with relaxation phenomena.

$$\varepsilon = \varepsilon_0 \text{ Sin } wt \tag{3}$$

$$\sigma = \sigma_0 \text{ Sin } (wt + \delta) \tag{4}$$

Sinusoidal excitations are uniquely informative because the derivative forms all have the same form as the excitation. Thus equation (1) becomes:

$$\sigma[a_m(iw)^m + \ldots a_1(w+a_0)]\text{expi}[wt+\delta] = \varepsilon[b_n(iw)^n + \ldots b_1(w+b_0)]\text{expi}wt \tag{5}$$

where $i = \sqrt{-1}$

$$\therefore \quad \sigma = \sigma_0 \text{ expi}(wt + \delta) \tag{6}$$

$$\varepsilon = \varepsilon_0 \text{ exp } iwt \tag{7}$$

Thus the complex modulus, $E^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_0 \text{expi}(Wt+\delta)}{\varepsilon_0 \text{exp } iwt} = E' + iE''$ (8)

Trigonometric manipulation gives

$$E^* = \frac{\sigma_0}{\varepsilon_0} [\text{Cos } \delta + i\text{Sin}\delta] \tag{9}$$

$$E^* = \frac{\sigma_0 \text{Cos}\delta}{\varepsilon_0} = \frac{i\sigma_0 \text{Sin}\delta}{\varepsilon_0} \tag{10}$$

but according to (8) $E^* = E' + E''$

$$\therefore \quad E^* = E' + E'' = \frac{\sigma_0 \text{Cos}}{\varepsilon_0} + \frac{i\sigma_0 \text{sin}\delta}{\varepsilon_0} \tag{11}$$

So $E' = \frac{\sigma_0 \cos\delta}{\varepsilon_0}$ (12) and $E'' = \frac{\sigma_0 \sin\delta}{\varepsilon_0}$ (13)

ie E' and E" are out of phase by 90° as shown in Figure 5.

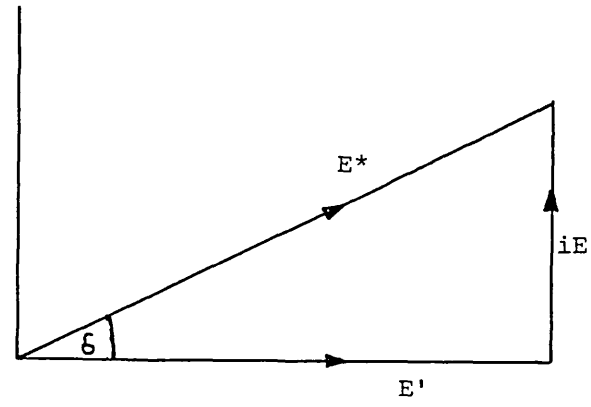


Figure 5 Vectorial Representation of Complex Modulus in Terms of Storage and Loss Modulus

The real part of the modulus, E', is called the storage modulus as it is associated with the elastic storage of potential energy, and its release in the periodic deformation. The imaginary part of the modulus, E", is called the loss modulus as it is related to the dissipation of energy as heat or sound when the deformation force is removed. The phase angle δ is given by:

$$\tan \delta = {}^{E''}/_{E'} \qquad (14)$$

As δ is the result of viscous flow it is often referred to as the internal friction coefficient or damping factor.

(e) Molecular Interpretations

Much research has been carried out on the relationship between molecular parameters and the dynamic mechanical behaviour of polymers[32]. DMTA expresses the dynamic mechanical responses of the polymer with respect to temperature and frequency and the resulting spectra show

relaxation processes of the polymer system at a given frequency as a function of temperature.

Typical DMTA spectra of an amorphous polymer are shown in Figure 6. Relaxation processes occur where the damping factor goes through a maximum when plotted against temperature, and when the elastic modulus (E') temperature curve has an inflection. The elastic modulus changes from 10^{10} Pa in the glassy state to 10^{7} Pa in the rubbery state. The α peak corresponds to the relaxation observed at the glass transition temperature. The β and γ peaks represent relaxations in order of decreasing temperature.

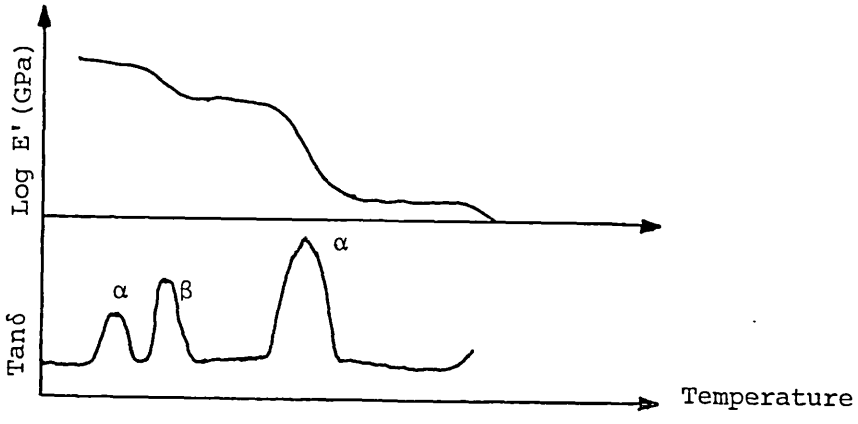


Figure 6 Typical DMTA Spectra of an Amorphous Polymer

The magnitude of the relaxation can be expressed in terms of their apparent activitation energy.

$$\tau = \tau_0 e^{\Delta HRT} \quad (15)$$

T = Temp (K)
τ_0 = relaxation time (O K)
τ = relaxation time (T K)
ΔH = Activitation energy
R = gas constant

If, $W = 1/\tau$ (16) and the same relaxation is measured at several frequencies then (16) may be substituted into (15) and the resulting equation solved simultaneously for

the chosen frequencies yielding the apparent activation energy. Practically, this is carried out graphically by plotting log frequency against inverse temperature. The gradient equals $\frac{\Delta H}{2.303} R$

PMMA, the most established "dental" polymer, has five relaxation processes[32]. However, the α and β relaxations yield most of the information about the dental material. The DMTA spectra are affected by several variables[32,35,37]: *stereoregularity, molecular weight distribution, degree of crosslinking, plasticiser content, polarity of polymer chain, flexibility of polymer chain, copolymerisation. filler content and filler/matrix morphology.*

The α relaxation

The α relaxation is associated with the glass transition temperature of the material at a given frequency. It is generally accepted that this relaxation is the micro-Brownian motion of molecular segments. At this temperature and frequency, segments of the chain move forming new conformational arrangements of the backbone of the polymer[37].

The α relaxation is dependent on free volume[34,38]. At the temperature of the α relaxation, or the glass transition temperature, there is sufficient free volume into which molecule segments can move in a micro-Brownian manner. Below this temperature there is insufficient free volume and so the only motion that can take place is rotational or vibrational. The rotational and vibrational motions are associated with the glassy state, and the

micro-Brownian movements with the rubbery state. Therefore, any factor which can reduce the temperature at which the free volume required for mico-Brownian motion is present will lower the temperature of the α relaxation, and hence the T_g, at a given frequency.

(i) Molecular weight distribution affects the temperature of the α relaxation. Since free volume around chain ends is taken to be greater than any other part of the chain because of packing, the larger the proportion of the lower molecular weight fraction, the greater the free volume and hence the lower the temperature of the α relaxation. However, above a molecular weight of 1.5×10^5 the temperature of the α peak becomes independent of molecular weight, as the concentration of chain ends is negligible[38]. Therefore a material with a greater concentration of lower molecular weight chains will have a T_g at a lower temperature and a smaller elastic modulus at this temperature. The length of the rubbery plateau region and tan δ value in the DMTA spectra will be spread across a greater temperature range as the molecular weight increases[35].

(ii) Stereoregularity also affects the temperature of the relaxation. . PMMA which is predominantly syndiotactic has a stiffer helical conformation than the isotactic form. This increased stiffness reduces its ability to move, thus, increasing the temperature of the α relaxation. Stereospecific syndiotactic PMMA has been prepared giving it a higher T_g than the conventional PMMA which is only about 60% syndiotactic [32].

(iii) Crosslinking agents reduce the ease of movement of the polymer molecules by creating large 3-dimensional networks. Thus, a greater free volume needs to be present to allow movement. This has the effect of shifting the α peak to higher temperatures with increasing crosslinks. At temperatures above T_g there is an increase in storage modulus with increase crosslinking[37]. This may be used as a gel index. The higher the value of the storage modulus the greater the gel content.

(iv) Plasticisers. The presence of plasticisers will shift the α relaxation to a lower temperature[32]. Once more this is explained in terms of free volume. The plasticisers reduce the temperature of the α relaxation by introducing free volume into the system. The final α relaxation temperature lies between the α relaxation temperature of the polymer and the plasticiser. Therefore, the greater the concentration of plasticiser in a polymer the lower the T_g.

(v) Copolymerisation. Copolymers may be classified as block or random. Block copolymers and polymer blends will show α relaxation for the individual polymers. Therefore, for a rubber reinforced denture base two α relaxations would be observed, one for the rubber, the other for the acrylic.

Random copolymers are far more complex. If a homogeneous copolymer is formed then a single, sharp, α relaxation is observed as all the chains have the same composition. The temperature of the T_g will lie between the values of the two homopolymers and will depend on

concentration. If a heterogeneous copolymer is formed the polymer chains will not all have the same composition and the α relaxation observed will be broad[37]. Heterogeneous copolymers are formed because of differences in reactivity of the monomers present. For example, if monomer A is more reactive than monomer B, then initially in the copolymer, A will tend to predominate, but at the final stages, B will be dominant monomer in the copolymer. The broadening of the relaxation peak can have great clinical significance as it means that part of the material may show properties characteristic of the glass transition temperature, such as low modulus, at temperature lower than anticipated. This would reduce the performance characteristics of the dental material.

(vi) Polymer Structure. Viscoelastic properties are greatly influenced by the structure of the polymer. Polymers with less flexible backbones reduce the propensity of the chain to flow, thus, increasing the temperature of the α relaxation. For example, a polymer chain is stiffened by the inclusion of aromatic rings. This is exemplified by Bis-GMA which has two aromatic rings in the backbone.

Addition of monomers with bulky side groups increases the steric hindrance of the molecule thus reducing its ability to move. Once more the effect is to increase the temperatures of the α relaxation[32]. However, in the case of n-alkylmethacrylate polymers there is a reduction in α relaxation temperature due to internal plasticisation[11].

Increased polarity will also increase the T_g due to the formation of secondary bonding. Once more this is due to the increased resistance to movement. Finally, it has been observed that the T_g reduces with increasing symmetry [39]. This is seen with poly (Vinyl Chloride) and poly (Vinylidene Chloride), the former has a greater T_g and is less symmetrical than the latter.

The β relaxation

The β relaxation was first observed in creep measurements by Lethersich [40] and has been reported by other workers using DMTA [41]. However, this relaxation has not been reported by workers in the dental materials field [35,36,41-4] The motion which induces the β relaxation is attributed to the rotational movement of in chain side groups [32]. Therefore, for PMMA the β relaxation is due to the rotational motion of the ester side chain [32]. Clearly, the energy required for rotational motion is less than that of micro-Brownian, and, so, the relaxation has a lower apparent activitation energy and is associated with the glassy state.

The β relaxation is very close to the α relaxation in methacrylate type polymers and is difficult to detect as it may merge and shoulder the α peak. However, using the PL-DMTA and altering specimen geometry, improved sensitivity may be obtained which allows the detection of the α peak. Nielsen observed that the β relaxation at 1 Hz for PMMA occurred at approximately 40°C [41].

Dimensional Stability

One of the most important criteria for a dental material is that it must be dimensionally stable. The greater the viscous component of the complex modulus the greater the propensity to flow, and thus, there is less dimensional stability. Given that $\tan \delta = {}^{E''}/_{E'}$ (14) the greater $\tan \delta$ at a given temperature and frequency, the greater the propensity to creep. However, as a dental material will be subjected to a range of temperatures varying between 0° to 60° C, a more realistic evaluation would be to measure the change in $\tan \delta$ across this temperature range as the propensity to creep for a system may vary depending on temperature.

Chapter 2: EFFECT OF MANUFACTURING METHOD ON REJECT RATE

2.1 INTRODUCTION

2.1.1 MOULDING SYSTEMS STUDIED

As stated in Chapter One, there are three types of moulding processes currently employed in the manufacture of polymeric artificial teeth - transfer moulding, compression moulding and pseudo compression moulding. This study involved the manufacture of a single component tooth and thus only two of the moulding systems, transfer moulding and pseudo compression moulding, are relevant. Compression moulding was not studied because the Wright Health Group did not have the tooling required to manufacture a single component tooth by this method. The aim of this section of work was to establish the optimum moulding parameters for each system.

The moulding parameters studied were:

Platen temperature.

Process pressure.

Dough condition time.

Monomer:Polymer ratio.

These variables were altered systematically to yield the minimum rejection for each system. The respective reject rates and corresponding cost effectiveness of the pseudo compression moulding and transfer moulding techniques were then compared. The most technically and commercially feasible system was selected for optimisation of the mechanical properties.

2.1.2 MONOCHROME-TYPE TOOTH TRANSFER MOULD DESIGN

The original transfer mould design used by the Wright Health Group (Appendix 1) had two major disadvantages when compared with the pseudo compression mould design (Appendix 2). Firstly,

high material usage; almost 300% greater than for the comparable compression mould and, secondly, the transfer mould cavity edges had a poor fit. This allowed excess material leakage, resulting in a pressure loss in the cavities and consequently, a very high level of moulding rejects. Therefore, a new transfer mould design was required which overcame the problem of high material usage and moulding rejection.

2.1.3 DEFINTION OF A REJECT

A reject tooth is one which has not matched the moulding, or mechanical property specification. Thus rejection may occur in two areas - (a) moulding faults, and/or (b) inferior mechanical properties. The quality of the moulding is a standard which is specified by the Wright Health Group and the mechanical properties standards are stated in BS3990 (1980), Acrylic resin teeth (Appendix 3).

(a) Moulding Rejects

An acceptable moulding is one which is free of - porosity (internal or external), warpage, sinks, scoring and cracks. The shade of the tooth must match the corresponding shade guide and must be constant throughout the tooth; no bleaching or pigment spotting must be present. The tooth must have a high lustre and possess a high degree of translucency so as to appear more realistic and life-like. Finally, the flash surrounding the mouldings must be thick enough to hold them together, but not too thick as to create difficulties in finishing the teeth.

(b) Rejection due to Inferior Mechanical Properties

The required mechanical properties of acrylic resin teeth are specified in British Standard 3990, 1980 (Appendix 3). The BS3990 requires that the teeth pass minimum levels of - dimensional stability, freedom from imperfections, freedom from harmful constituents, retention of surface finish, ability to repolish, hardness and resistance to blushing, distortion and crazing.

If teeth fail any of these specifications they are rejected.

2.2 EXPERIMENTAL

2.2.1 INVESTIGATION INTO THE RELATIONSHIP BETWEEN PLATEN TEMPERATURE AND INTERNAL POROSITY IN COMPRESSION MOULDING

Method

Rings of material were chosen at random from standard production prepared in the Mixing Department and loaded into a 4xu mould. The platens on the pilot plant press were regulated to specific temperatures by measuring the surface temperature of the platens with an electrical thermometer and thermocouple.

A sample size of 160 teeth, processed at various temperatures, was analysed for internal porosity.

Benzoyl peroxide concentration	0.5% weight of the polymer present
Monomer:Polymer ratio	1:2.7
EGDMA concentration	6% (vol/vol) of liquid
Mix time	2 mins
Material Conditioning Time	30 mins at 25°C
Pressure	5 tons
Time Cycle	4 mins 30 secs heating, 4 mins 30 secs cooling
Mould	4xu
Temperatures	80°C, 100°C, 120°C, 140°C, 160°C

Results

Platen Temp	% Teeth with Internal Porosity
80°C ± 2°C	Soft Teeth
100°C ± 2°C	0
120°C ± 2°C	6.25%
140°C ± 2°C	56.25%
160°C ± 2°C	100%

Internal porosity is absent from the teeth if the platen temperature is kept below 120°C. However, if the temperature is lowered to 80°C, the teeth produced are soft.

2.2.2 DETERMINATION OF THE HEATING RATE OF THE DOUGH INSIDE THE CAVITY OF A MOULD DURING COMPRESSION MOULDING

Method

A standard production ring of dough was loaded into a 1x type mould. A thermocouple wire was embedded in the dough so that during processing it would locate into the centre of a large tooth. The thermocouple was connected to an electrical thermometer which in turn was connected to a flat-bed recorder. The digital thermometer had an output of 1mV per °C, the flat-bed recorder was set to a full scale deflection of 20mV which corresponded to 200°C. The platens on the press were set to temperatures of 100°C, 110°C, 115°C, 120°C and 130°C.

During each run the same cavity was used. From the time-temperature profiles, the time taken to reach the boiling point of MMA, 100.3°C, was determined.

Results

Platen Surface Temp	Time to reach 100.3 C/Secs	Time for Conversion/Secs	% Internal Porosity
100°C ± 2°C	-	270	0
110°C ± 2°C	190	190	0
115°C ± 2°C	178	178	0
120°C ± 2°C	125	125	6.3
130°C ± 2°C	102	102	31.3

Results show that 178 seconds allowed sufficient time for conversion of monomeric MMA to less volatile material. A possible conversion time of 125 seconds is insufficient to allow all of the monomer to convert before its boiling point is reached, thus any monomer left boils off resulting in internal porosity. The smaller the conversion time the greater the incidence of porosity as more monomer will be present when its boiling point is reached.

2.2.3 DETERMINATION OF OPTIMUM PLATEN SURFACE TEMPERATURE WHICH WILL CREATE A HEATING RATE THAT PRODUCES SOLID TEETH FOR ALL MOULD SIZES

Method

This experiment used the same method as 2.2.2 except the temperature was fixed at 115°C and the mould sizes used were 1x, 18x, 20x and 4x. The conversion times and incidence of internal porosity were noted.

Results

Mould Size	Platen	Time to reach 100.3 C/secs	Conversion time/secs	Internal porosity
1x	115 ± 2	175	175	0%
18x	115 ± 2	250	250	0%
20x	115 ± 2	250	250	0%
4x	115 ± 2	230	230	0%

A platen temperature of 115 ± 2°C allows sufficient conversion time for the monomer to be converted to less volatile material in all mould sizes.

2.2.4 ESTIMATION OF AVERAGE REJECTION LEVEL FOR PSEUDO COMPRESSION MOULDING SYSTEM

Method

Sixteen teeth were collected from standard production 1x, 2x, 18x and 4x moulds, every fifteen minutes from ten days production. This gave a total sample population of 38,400. Every tooth was analysed for - external porosity, sink marks and dull finish. The percentage rejection for each mould was calculated and the mean of these percentages was then found. Other data calculated was the range and standard deviation. These indicated the variability of rejection.

Each day 32 teeth were tested for compliance to BS3990 (1980) (Appendix 3).

Results

(a) Average rate of rejection at moulding

Mean = 18.58%

Standard deviation = 5.04

Range = 9.37% - 31.25%

	2x Mould	1x Mould	18x Mould	4x Mould
Mean	14.98	17.44	19.55	22.40
Standard deviation	6.38	7.70	6.40	5.0

(b) Compliance to BS3990 (1980)

All teeth failed the test for resistance to crazing, blushing and distortion, but passed all other tests.

2.2.5 DETERMINATION OF OPTIMUM MATERIAL CONDITION FOR PSEUDO COMPRESSION MOULDING

Method

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:polymer ratio	1:2.7
EGDMA concentration	6% (vol/vol) of liquid
Mix time	2 mins
Pressure	4 tons
Time Cycle	4 mins
Mould	4 xu
Temperature	115°C ± 2°C
Conditioning Times	30 min intervals from 0 to 420 mins

Results

Time (mins)	External Porosity (%)	Sink Marks/dullness/ underpacking (%)
0	18.75	31.25
30	25.0	25.00
60	0	18.75
90	0	12.50
120	0	25.00
150	0	25.00
180	0	31.25
210	0	18.75
240	0	12.50
270	0	18.75
300	0	25.00
360	0	37.50
390	25.0	75.00
420	31.25	68.75

Material which had been conditioned from 60 to 360 minutes afforded the lowest reject rate. The rejection during this period appeared to be random.

2.2.6 DETERMINATION OF THE OPTIMUM CROSSLINKING AGENT CONCENTRATION TO ELIMINATE CRAZING IN PSEUDO-COMPRESSION MOULDED TEETH

Method

It has been reported[6] that crazing can be eliminated by increasing the concentration of crosslinking agent EGDMA. Thus the concentration of EGDMA in the liquid content of the dough was increased until crazing could not be seen after the teeth were subjected to the resistance to crazing, blushing and distortion test specified in BS3990 (1980). The crosslinking agent was added in 6%, 10%, 20%, 30%, 40%, and 50% volume of the liquid component of the dough. The dough was then processed in the same fashion as experiment 2.2.1.

Results

Concentration of EGDMA (% volume in liquid)	State of the teeth after crazing, blushing and distortion test specified in BS3990 (1980)
6%	Crazing present
10%	"
20%	"
30%	"
40%	No crazing
50%	No crazing

By the addition of 40% by volume of EGDMA to the liquid component of the dough crazing is eliminated.

2.2.7 NEW TRANSFER MOULD DESIGN

Aim

The aim of this experiment was to design a transfer mould which would have a reduced transfer pot volume and therefore have a lower material usage.

Method

The cross-sectional area of the transfer pot was reduced so that only the area directly above the transfer sprews was exposed to the material. The central portion was built up with an alloy plated with hardened stainless steel. (Appendix 1)

The surface imperfection reject rate and rate of compliance to BS3990 (1980) was calculated using a sample size of 160 teeth. The effect of altering temperature, pressure, material condition and monomer:polymer ratio on the defect rate were determined and compared using Student's t-test (see Appendix 4).

Results

(a) Effect of Changing Temperature

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:polymer ratio	1:2.7
EGDMA concentration	10% (vol/vol) of liquid component
Mix time	2 mins
Condition time at 25°C	40 mins
Pressure	6 tons
Time cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperatures	145°C, 155°C, 165°C, 175°C

(b) Effect of Changing Pressure

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:polymer ratio	1:2.7
EGDMA concentration	10% (v/v) of liquid component
Mix time	2 mins
Condition times at 25 °C	40 mins
Pressures	4.5 tons, 5.5 tons, 6.5 tons
Time Cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperature	165 °C

(c) Effect of Changing Material Condition Time

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:polymer ratio	1:2.7
EGDMA concentration	10% (v/v) of liquid component
Mix time	2 mins
Condition times at 25 °C	30 mins, 40 mins, 60 mins, 90 mins.
Time cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperature	165 °C

(d) Effect of Changing Monomer:Polymer Ratio

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:polymer ratio	1:2.7 and 1:2.3
EGDMA concentration	10% (v/v) of liquid component
Mix time	2 mins
Condition times at 25°C	40 mins, 60 mins and 90 mins
Time Cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperature	165°C

Results

(a) Effect of Changing Temperature

Temperature (°C)	Mould reject rate (%)	Compliance to BS3990 (1980)
145	100	Failed - High crazing
155	100	Failed - High crazing
165	50	Failed - Medium crazing
175	67	Failed - Low crazing

Teeth produced at lower temperature had greatest amount of crazing.

(b) Effect of Changing Pressure

Pressure (tons)	Mould reject rate (%)	Compliance to BS3990 (1980)
4.5	100%	Failed - High crazing
5.5	100%	Failed - Medium crazing
6.5	50%	Failed - Low crazing

Teeth produced at a lower pressure had less of a tendency to craze.

(c) Effect of Changing Material Condition Time

Time of conditioning at 25 °C (min)	Moulding reject rate (%)	Compliance to BS3990 (1980)
30	54.1	Failed but low crazing
40	47.5	"
60	43.7	Failed but medium crazing
90	38.0	"
120	41.0	Failed with high crazing

Teeth produced from material which was more elastic had a greater propensity to craze.

(d) Effect of Altering Monomer/Polymer Ratio

Monomer/ polymer ratio	Material condition time (mins)	Moulding reject rate	Compliance to BS3990 (1980)
1:2.7	40	47.5%	Failed crazing only
1:2.3	40	81.5%	"
1:2.7	60	43.7%	"
1:2.3	60	65.9%	"
1:2.7	90	38.0%	"
1:2.3	90	54.3%	"

Teeth produced from 1:2.3 ratio crazed less.

2.2.8 INVESTIGATION OF THE EFFECT OF IMPROVING CAVITY EDGE FIT ON THE DEFECT RATE OF TEETH PRODUCED BY THE NEW TRANSFER MOULD

Aim

Results from experiment 2.2.7 (d) indicated that the defect rate might be reduced if the cavity pressure could be maintained by decreasing material flow. The object of this experiment was to investigate the effect on reject rate of improving cavity edge fit and finish.

Method

The quality of cavity edge fit is estimated by coating the edges of one half of the mould with a blue dye and then closing the mould. The mould is then opened. A mould with a good fit is one where both edges are blue. Areas which have no dye are low spots and the edges may be ground until there are no low spots. The edges were highly polished using a diamond polish. The effects of changing temperature, pressure and material condition on surface imperfection defect rate and compliance to BS3990 (1980) were determined.

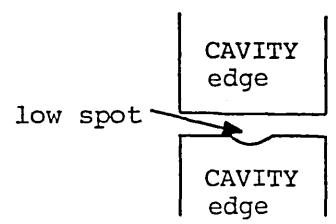


Figure 7 low spot: allows material leakage

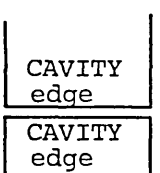


Figure 8 After grinding: perfect finish

Method

(a) Effect of Changing Temperature

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:Polymer ratio	1:2.7
EGDMA concentration	10% (v/v) of liquid component
Mix Time	2 mins
Condition Time at 23°C	40 mins
Pressure	4.5 tons
Time Cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperatures	145°C, 155°C, 165°C, 175°C, 185°C

Results

(a) Effect of Temperature

Temperature	Moulding reject rate (%) (Standard deviation in brackets)	Compliance to BS3990 (1980)
145°C	81.25 (1.49)	Failed on crazing
155°C	48.75 (1.13)	"
165°C	6.25 (0.816)	"
175°C	1.25 (0.422)	"
185°C	3.125 (0.707)	"

Tests of significance using Student's 't' test gave the following results:

175°C v's 185°C: No significant difference in mean ($p \leq 0.05$)

175°C v's 165°C: Significant difference in mean ($p \leq 0.05$)

165°C v's 185°C: No significant difference in mean ($p \leq 0.05$)

Method

(b) Effect of Changing Pressure

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:Polymer ratio	1:2.7
EGDMA concentration	10% (v/v) of liquid component
Mix Time	2 mins
Condition Time at 25°C	40 mins
Pressures	3.5 tons, 4.5 tons, 5.5 tons, 6.5 tons
Time Cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperature	175°C

Results

(b) Effect of Changing Pressure

Pressure (tons)	Moulding Reject Rate %	Compliance to BS3990 (1980)
3.5	7.5 (0.42)	Failed crazing
4.5	1.8 (0.483)	"
5.5	2.8 (0.675)	"
6.5	2.5 (0.699)	"

Results from statistical comparison of means ($p \leqq 0.05$) showed that the defect rate at 3.5 tons pressure was significantly greater than that at higher pressure. There was no significant difference in the means of the defect rate of teeth produced at 4.5, 5.5 and 6.5 tons.

Method

(c) Effect of Changing Material Condition Time

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:Polymer ratio	1:2.7
EGDMA concentration	10% (v/v) of liquid component
Mix Time	
Conditioning times at 25°C	40 mins, 60 mins, 90 mins and 120 mins
Pressure	4.5 tons
Time Cycle	4 mins heating and 4 mins cooling
Mould	20 xu
Temperature	175°C

Results

(c) Effect of Changing Material Condition Time

Material Condition (mins)	Moulding Reject Rate (%)	Compliance to BS3990 (1980)
40	2.08	Failed Crazing
60	2.08	"
90	2.73	"
120	5.0	"

Statistical significance testing of the mean values of the defect rate using Student's t-test indicated that the only significant difference in means ($p \leq 0.05$) was between the materials conditioned for 40 and 60 minutes compared to the material conditioned at 120 minutes. The latter had an average defect rate significantly greater than the materials conditioned for 40 and 60 minutes.

2.2.9 DETERMINATION OF THE OPTIMUM CROSSLINKING AGENT CONCENTRATION TO ELIMINATE CRAZING IN TRANSFER MOULDED TEETH

Method

From Section 2.2.6 it is seen that increased temperature, reduced pressure and material condition only reduce the propensity of crazing. To fully eliminate crazing the concentration of crosslinking agent must be increased.

The concentration of EGDMA in the liquid component of the dough was altered and the teeth produced were tested for compliance to BS3990 (1980).

Benzoyl peroxide concentration	0.5% (w/w) of PMMA
Monomer:Polymer ratio	1:2.3
Mix Time	2 mins
Material condition time	40 mins
Pressure	4.5 tons
Time cycle	4 mins heating and 4 mins cooling
Temperature	175°C
% vol EGDMA in liquid	6%, 10%, 20%, 25%, 30%

Results

Concentration of EGDMA (% vol in liquid)	State of the teeth after crazing, blushing and distortion test specified in BS3990 (1980)
6	Failed Crazing
10	"
20	"
25	Passed Crazing
30	"

2.2.10 CHARACTERISATION OF THE RHEOLOGICAL PROPERTIES OF MMA/PMMA DOUGH

Method

MMA/PMMA doughs are non-ideal materials. They exhibit Non-Newtonian and elastic behaviour, ie they are viscoelastic. The proportion of these two behaviour types possessed by a dough varies with time. The extent to which they vary with time also depends on formulation, temperature and quality of raw materials. The viscoelastic behaviour of the dough was measured by determining the dynamic viscosity and storage moduli of the dough against time, using a controlled stress rheometer* in the oscillation mode.

The instrument measures G' across a frequency sweep of 0.01 Hz to 10 Hz at 23 °C. The measurements were carried out 10, 40 and 90 minutes after mixing. All samples were conditioned at 25 °C. For each sample, G' was plotted against frequency. The maximum and minimum value of G' for each sample was noted and compared.

Monomer:polymer ratios of 1:2.7 and 1:2.3 were studied.

*Controlled Stress Rheometer: Carrimed Instruments, Dorking, Surrey

Run details

Sample reference:	IM01
Run number:	01
Operator identity:	IM
Plate geometry:	2 cm parallel plate
Sample notes:	
Procedure:	04 ian2
Liquid density:	1.000 g cm-3
Machine inertia:	25.30 Micro N.m sec-2
Measurement system factor:	0.6366
Fluid density factor:	0.3333
Measurement system gap:	10000 Micro m
Auto amplitude:	5.000 milli radians
Oscillatory mode:	Frequency sweep
Temperature:	23 Deg°C
Torque:	40000 Micro N.m
Start frequency:	10.00 Hz
Final frequency:	0.01000 Hz
Number of points:	30
Generating software:	4.3 OSCILLATION

Results

Monomer:Polymer ratio	Time from Mixing	G'min (Pa)	G'max (Pa)	η'min (Pa.S)	η'max (Pa.S)
1:2.7	10	16,650	30,240	322.5	372,800
1:2.7	10	2,552	5,203	66.5	137,200
1:2.7	40	119,200	455,650	1,232	1,120,500
1:2.3	40	89,020	371,000	1,053	969,000
1:2.7	90	*	*	*	*
1:2.3	90	*	*	*	*

* The instrument did not produce consistent data due to slippage

From the data and Figure 9 the following observations may be made:

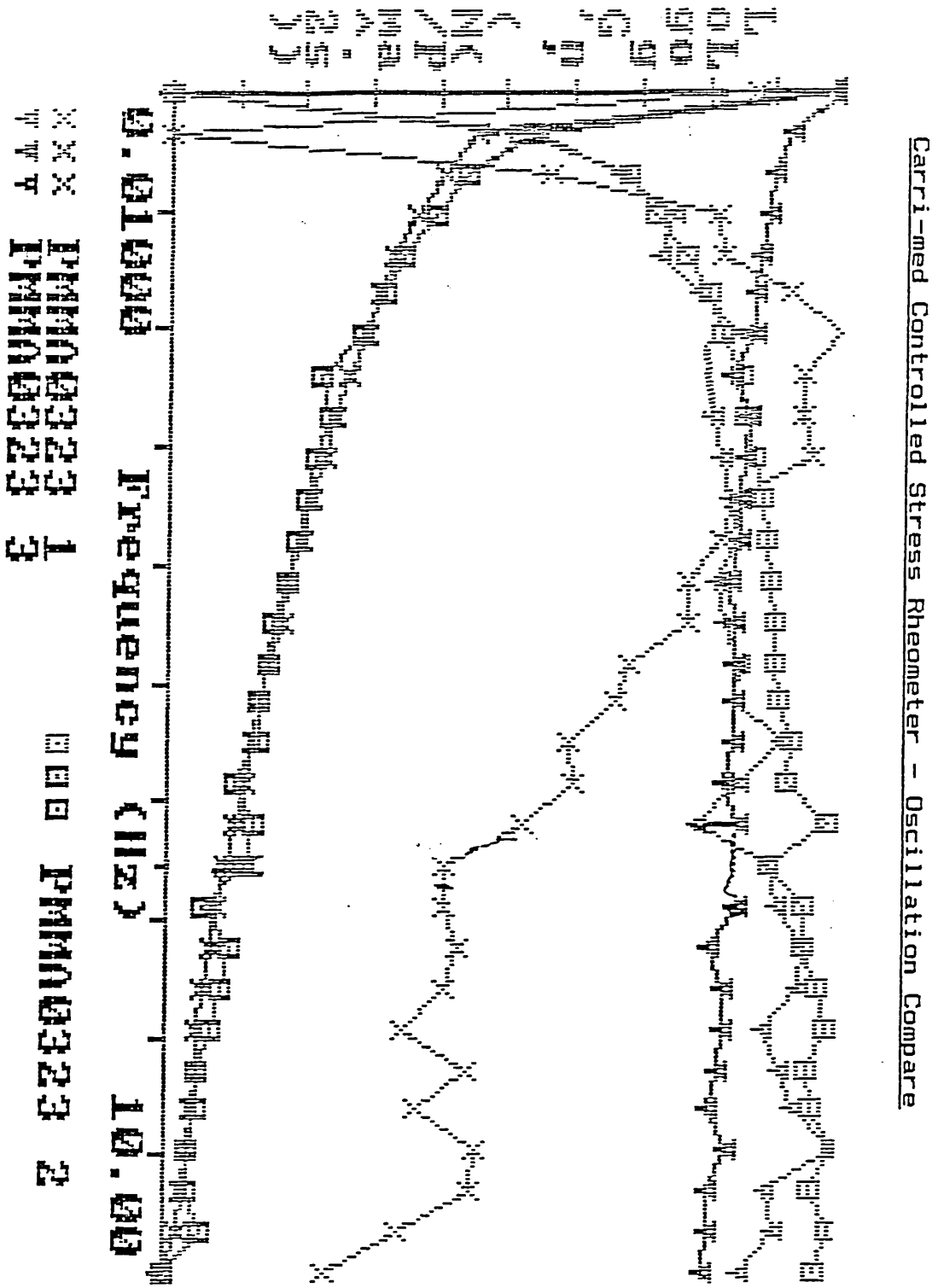
(i) If the monomer content is increased the viscous behaviour is greater when measured at a set time t.

(ii) Structure is broken down at higher frequencies 10 minutes after the mixing.

(iii) As frequency of applied strain is increased the viscosity reduces. Thus, the material is shear thinning.

(iv) The rigidity (elastic behaviour) of the material increases with time across all frequencies.

(v) Correspondingly the viscosity also increases as the degree of viscous behaviour decreases.



PMMA 03231 was tested 10 minutes after mixing

PMMA 03232 was tested 40 minutes after mixing

PMMA 03233 was tested 90 minutes after mixing

Figure 9 Comparison of Rheological Properties of Dough with Time

2.3 DISCUSSION

2.3.1 PSEUDO COMPRESSION MOULDING SYSTEM - EVALUATION OF OPTIMUM MOULDING CONDITIONS

Conditions and Moulding Specification Rejection Rate

The aim of this section of the study was to investigate the relationships between three process variables and the rejection rate, and thus establish those moulding conditions which afforded the lowest reject rate. The variables investigated were:

Temperature.
Material condition time.
Polymer:Monomer ratio.

The faults which result in rejection at moulding arise from (a) internal porosity and (b) surface imperfection such as sink marks and external (visible) porosity and dullness.

(a) Internal Porosity

The heat of polymerisation of MMA is 57.7 $KJmol^{-1}$ [44] This heat of polymerisation and/or uncontrolled production heating rates can be sufficient to lead to vapourisation of volatile monomeric materials before they have been converted to molecules of a higher molecular weight and hence a less volatile polymer[44]. Skinner and Philips[3] have reported that traces of impurities which become entrapped in the dough, either before or during polymerisation, may lower the boiling point of the monomer. Purity is therefore of the utmost importance.

Impurities are also detrimental to the polymerisation process and hence the mechanical properties. Various methods have been employed to eliminate the boiling of

monomer and thus remove all of gaseous porosity[3]. These involve such expedients as:

Careful regulation of heat.
Moulding-in a superimposed layer.
Increasing the content of less volatile constituents.

(i) Platen temperature and internal porosity

Experimental evidence (see section 2.2.2) has shown that the heat of polymerisation is dissipated by the polymeric content in the mould. There was no sharp increase in temperature over a short period of time, which is characteristic of the build up of hot spots. Even in the mouldings which did have internal porosity the thermocouple did not detect any sharp rises in temperature. Therefore the only source of heat was the moulding press platen. The temperature of the platen determined the heating rate of the dough in the mould. If the heating rate was too high then the temperature of the mould reached the boiling point of the MMA before the monomer was converted to polymer. It was established that if the temperature was decreased then the internal porosity was eliminated as there was sufficient time for the monomer to convert to a less volatile polymeric material. The internal porosity was therefore gaseous porosity caused by the volatilisation of MMA. The porosity was internal because the vapourised material was travelling to a cooler area of the moulding away from the external heat source.[45]

(ii) Mould size, platen temperature and internal porosity

To make different types and sizes of teeth, different moulds are required and mould size affects the conduction of heat from the platen to the dough. Therefore different mould sizes will have different heating rates under identical process temperatures. It was found that at sufficiently high temperatures - eg 130°C - the larger teeth possessed internal porosity but smaller teeth moulded in a smaller mould had no internal porosity. Hence, when the boiling point of the monomer is reached in the larger cavity, monomer will still be present resulting in internal porosity. However, in the smaller tooth no monomer is left when the boiling point is attained. If the temperature is increased sufficiently, eg above 150°C, the rate of heating will be so great that internal porosity will be present in all teeth. Similarly, if the temperature was reduced to 80°C the teeth produced were soft. Within the given time cycle insufficient energy had been supplied to polymerise the MMA to a degree which results in a molecular weight distribution which yields the required mechanical properties[21]. It was found that by adjusting the platen temperature to 115±2°C, all teeth produced were solid throughout their structure regardless of the size of the tooth. Therefore by controlling the heating rate the monomer was afforded enough time to convert to less volatile polymeric material before its boiling point was reached, thus eliminating gaseous or internal porosity.

(b) Surface Imperfections

(i) Average rejection level

Results from a random sample of 38,400 teeth, moulded from mould sizes 4x, 18x, 1x and 2x, showed the average level of rejection through the surface imperfections of surface porosity, dullness and sink marks to be 18.85% (with a standard deviation of 5.04). The standard deviation is a simple method of judging how representative any average is of its population. In general the smaller the standard deviation compared to the size of the average the more closely the items in the population are clustered around the average and, therefore, the more representative the average is of that population[46]. Rejection due to surface imperfections was very variable with a standard deviation being 5.04. This means that the bulk of the results lay between 13.81% and 23.89%. This high and variable value is unacceptable for two commercial reasons: product confidence and cost. It has been suggested that the post-moulding processes will improve the quality of the teeth with sink marks and dullness by smoothing the edges around a sink mark and polishing a dull surface[47]. However, these teeth never match the quality of perfect mouldings, and if they are still rejected after more processing the cost of the reject has increased, and a greater loss is incurred.

(ii) Rejection rate and mould size

The rejection rate for four different mould sizes was determined. The mould which had the greatest volume gave the highest reject rate and the mould with the smallest volume produced the lowest number of defective mouldings. Assuming that the ring of dough placed in each mould size is identical it may be argued that as each mould is closed the pressure inside the cavity will be greater in smaller volume moulds than in the larger due to the excess of material[45](Figure 10). If there is a pressure drop (caused by polymerisation shrinkage) the excess material will flow to the area of lower pressure. In the larger moulds there is not such a great excess and, so, if there is a pressure drop inside a cavity the pressure difference is not significant enough to cause any excess material to flow into the cavity.

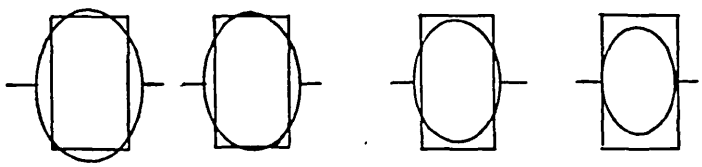
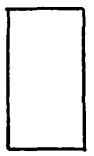


Figure 10

Effect of Cavity and Material on Cavity Pressure



= Material

(iii) Possible causes of rejections

Methacrylate polymerisations are accompanied by liberation of heat and a decrease in volume; both of these factors may strongly affect the production process and reject rate. As MMA is polymerised there is a decrease in volume of 21%[44]. However, in the dough technique practiced by the Wright Health Group the monomer content only accounts for 27% of the total volume. Therefore the system will only reduce in volume by approximately 5.7%. It is this shrinkage which causes surface porosity or contraction marks[45]. This is overcome by using excess material which compensates for the reduction in material volume. Dullness on the surface of the tooth may be due to trapped air which spreads as a thin layer between the tooth and mould surface. This is why the tooth face does not reproduce the high lustre of the mould surface. The source of the air is the ring itself. The air is trapped in the material during the preparation of the "salami" of dough. The occurrence of the air pockets is purely random and the ability of the air to be evacuated during moulding must depend on the quantity of air, the rheology of the dough itself, and the effective pressure in the cavity. The volume of air present in the ring must also affect the pressure in the cavity. The more air in the ring the less material will be present, Therefore when the air is removed there will be a reduction in volume and a corresponding reduction in cavity pressure. Hence, there will be no compensation for the polymerisation shrinkage and this will yield surface defects. The random

occurrence and variable concentration of air entrapped in the ring would explain the high variability in surface imperfection rejection rate.

(iv) Effects of process variables on rejection rate

Pseudo compression moulding relies on the ability of the material to create a pressure inside each cavity and have excess material in the mould to flow into the cavity to compensate for polymerisation contraction. Therefore, the rheology of the materials and factors which affect its rheology are crucial in determining the quality of the moulding. Increasing temperature will increase the flow properties but as the temperature must not exceed 115°C, due to the occurrence of internal porosity above this value, temperature is fixed for this moulding system. Material condition or dough stage is very important in determining the rheological behaviour of the material. During the early stages of the monomer:polymer interaction the dough has a low viscosity and a relatively low elasticity. Therefore, it will behave more like a viscous fluid which has little network structure. What structure is present is readily broken down by applying a deformation at relatively low frequencies (1-10 Hz). In this state the material possesses a high degree of flow and when pressure is exerted on it by the closing of the cavity the material flows out of the mould. Such underpacking results in a lack of pressure and so external porosity, sink marks and dullness arise from the inability to counteract the polymerisation shrinkage, and remove air entrapped in the ring of dough.

Both viscosity and elasticity of the dough increase with time. The monomer and polymer interact to give a structure which is now more rigid and elastic in behaviour. The propensity for viscous flow is reduced, whilst elasticity has increased. This is observed because the material has a more interlinked structure which will prevent continuous flow beyond that allowed by the elasticity of the sample. The only case in which the dough will flow beyond these limits is when failure of the structure occurs[48]. In this state the material may become so rigid that it will not flow to fill all of the cavity, thus affording an under-formed tooth. With reduced flow properties the material will not be as efficient at compensating for polymerisation shrinkage by flowing to an area of reduced pressure. Finally, if the material is more rigid it will prove more difficult to remove entrapped air in the ring from the cavity. Thus a dough which contains degrees of viscous and elastic components which lie between the two limits discussed above will possess the rheological properties which are necessary to fill the mould and maintain sufficient material in the cavities whilst creating enough pressure to eliminate surface imperfections.

The possible reason for the observed change in the rheological properties of the materials with time is that two processes may occur when the monomer and polymer interact. Firstly, monomer molecules slowly diffuse into the polymer to produce swollen gels. The gels partially

disintegrate over a period of time by dissolution of the polymer molecules. As the polymer molecules dissolve they uncoil and the viscosity of this solution increases[39]. Since there is a great excess of polymer a saturated solution may be formed and at this point no further dissolution will occur. Thus far, the viscosity of the system will have increased due to the polymer solution and, also, to any coalescence of swollen polymer gels. As the gels interact the matrix will be transformed from a slurry to a coalesced gel structure. This gel will have a more interlinked structure than the slurry and it's elasticity is also increased. However, as the dental PMMA systems are heterogeneous, the dough will consist of a gel with polymer beads dispersed throughout. The elasticity of the system may increase because the extended polymer molecules in solution diffuse throughout the gel forming inter-connections between the undissolved polymer chains. The processes of swelling, dissolution and diffusion are temperature and time dependent. This explains why the dough process may be retarded by reducing the ambient temperature or increased by raising the ambient temperature. Altering the monomer:polymer ratio will affect the rheological properties of the dough. If the ratio is increased in favour of the monomer, the dough will take longer to develop a more elastic and rigid structure than a dough with less monomer. This phenomenon may be due to extra free volume created in the structure by the increased concentration of small monomer molecules[49], and there will be less bead present to fill the gel.

Clearly the monomer:polymer ratio affects the flow behaviour of the dough and if a "wetter" dough is processed at the same time from mixing as a "dry" dough, then the rate of rejection will differ due to differences in the structure of the dough at that point in time.

It was found that a process window existed with regard to material rheology. Inside this window the incidence of surface porosity was reduced, but the rate of contraction marks and dullness were still relatively high and very variable. A possible reason for this observation is that the rings contain varying amounts of air which cause pressure in the cavity. Mix homogeneity may also affect the variability of reject rate. If the preformed rings have different monomer/polymer concentration ratios they will exhibit different rheological properties which would result in changing moulding characteristics from the same batch of dough.

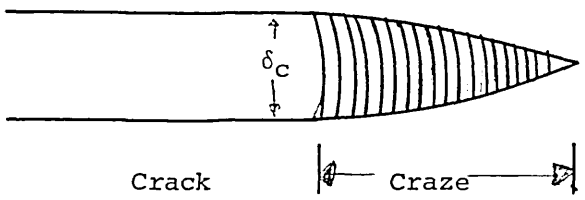
2.3.2 PSEUDO COMPRESSION MOULDED TEETH. REJECT RATE CAUSED BY FAILURE TO COMPLY WITH BS3990 1980, ACRYLIC RESIN TEETH

Teeth moulded by the Wright Health Group usual conditions using their standard formulation passed all the tests in the specification except resistance to crazing, blushing and distortion. The teeth all failed due to presence of crazing in the moulding. When a polymer is processed three types of residual stresses may be induced [50]. These stresses may arise from: quenching stresses, frozen-in molecular orientation and configurational volume changes.

Clearly there are configurational volume changes due to the change of phase from liquid to solid when MMA is polymerised. The rate at which the material is quenched from moulding temperature to the glass transition temperature also affects the levels of residual stresses. If the material is cooled too quickly, to below its glass transition temperature (Tg), the molecules will be frozen in an uncoiled state which creates residual stresses as the molecules are more stable in the coiled state. The uncoiling of the polymer molecules may result from heating above the Tg of the polymer, or induced by the nature of the process; for example,a process involving high shearing action will cause the molecules to orientate themselves in a particular fashion [50].

As the process of pseudo compression moulding is a low shear process [51] and the fact that the temperature only edges above the Tg of PMMA 105℃ [52] it may be predicted that the major source of residual stresses is due to the configurational volume change during the curing process.

Absorption of water and monomer into a polymeric structure increases the free volume of the systems[44]. This increase in free volume allows segments of the molecules to relax and thus relieve themselves of residual stress. It has been stated [53] that as the molecules lose the residual stress they are mechanically transformed and they "bridge" the microvoids of free volume. In doing this the transformed molecules will have a different refractive index from other polymer molecules and appear to the eye as small cracks. They are not cracks but crazes. It is believed that these crazes are precursors to cracks because they may act as crack growth initiators.



Craze becomes a crack when craze width is greater than a critical value δ_c

Figure 11 Crazing

Reduction in the amount of unrelaxed or residual stress will improve the mechanical properties of the moulding[50]. Residual stresses and thus crazing may be overcome either by locking in the orientation of the molecules and thus not allowing the molecules to manoeuvre across free volume or by allowing the molecules to relax and relieve themselves of the process-induced strains during the process itself. The latter approach would involve either increasing the process temperature or increasing the time cycle. Due to the fact that an increased temperature would cause internal porosity, and an increased time cycle is not economically feasible it was decided to attempt to eliminate crazing by reducing the propensity of the network to flow. This flow restriction was achieved by increasing the elasticity of structure. The result of this is that although the monomer and/or water (absorbed during test) has increased the free volume of the system, the stressed molecules cannot lose the residual stress

because they cannot move into the free volume and undergo a relaxation process. Increasing the rigidity of the structure is achieved by increasing the crosslinking agent concentration of the formulation from 6% (vol of liquid component) to 40%. At 40% EGDMA no crazing was observed. Such a measure is also used in the preparation of denture base. However, in denture base, these high concentrations of EGDMA are not required to combat crazing[2,54]. This emphasises the contribution quenching stresses play as the denture base processing involves a slower cooling rate, thus allowing for the relaxation of the residual stresses.

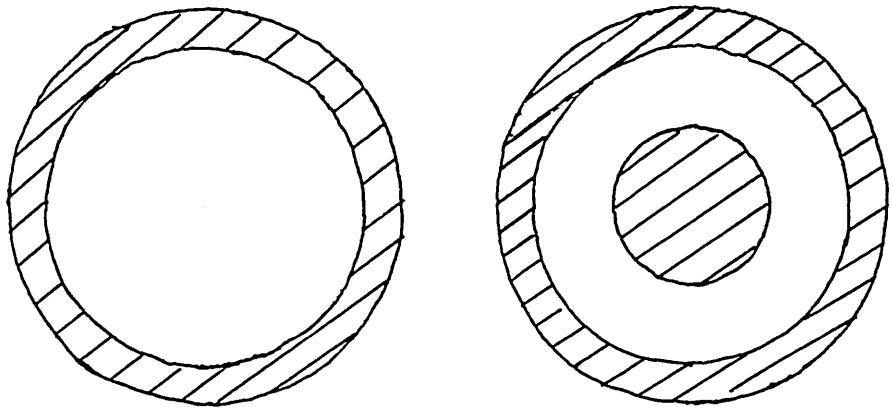
2.3.3 MONOCHROME TOOTH TRANSFER MOULD DESIGN

The two key areas of improvement for the transfer mould design were (a) material usage and (b) cavity pressure.

(a) Material Usage

The weight of dough used for a single transfer moulding was 30g, compared to a 10g ring used in the pseudo compression moulding. This would result in an an increased material usage of approximately 200%, if the current transfer and pseudo compression moulding systems were compared.

To enable a reduced quantity of material to be used in the transfer mould a new transfer pot was designed (Figure 12).



Plan of old design Plan of new design

Figure 12 New Transfer Pot Design

Key denotes metal

denotes moulding material

The modified transfer pot had a material requirement of 15 g (which would result in only a 50% increased material usage compared to the pseudo compression technique). Given that pressure is defined as force per unit area, the effective pressure applied to the material in the new transfer pot must be greater than that applied to the material in the old design because of the reduction in area upon which the force from the press is applied. Therefore, modifying the transfer pot design had two clear advantages - it reduced material usage and increased the effective pressure applied to the material in the transfer pot.

(b) Cavity Pressure

Transfer moulding in the Wright Health Group is employed in the manufacture of polychrome, two component teeth.

The compression moulded incisal layer acts as a polymeric 'gasket' and improves the seal between cavity edges and so almost eliminates any pressure loss from the cavity. If this 'gasket' is removed there is an excessive loss of pressure due to material leakage and this yields rejects at moulding due to sink marks, porosity and dull finish. Prior to improved alignment and polishing of cavity edges, the reject rate was found to be 18% and 69% on the front and back surfaces of the tooth respectively. However, after treatment the defect rate was cut to 50% on the back of the tooth and eliminated completely on the front.

Therefore, by improving the alignment and surface finish of the cavity edges a better seal and thus an increased cavity pressure was afforded. Obviously a rejection rate of 50% was unacceptable and so the optimum moulding conditions for the new mould design were evaluated.

2.3.4 TRANSFER MOULDING SYSTEM - EVALUATION OF OPTIMUM MOULDING CONDITIONS AND THE RESULTING MOULDING SPECIFICATION REJECTION RATE

The new design of transfer mould had reduced the process material usage by 50%. If the system could be optimised and the rejection rate reduced to consistently minimal values, then this system would be more cost effective than the pseudo compression method, because the majority of the cost of production in the tooth is incurred as labour costs - not material costs. A transfer moulding involves injecting the correct amount of material into the mould at the proper

temperature and pressure which will form and cure a tooth in the shortest possible time. At moulding there is a complex relationship between temperature, material viscoelasticity, pressure and time cycle. These variables will all affect the final quality of the moulding. As stated earlier (1.3.4) the flow of material during the moulding process must be controlled if perfect mouldings are to be produced. Therefore, the effect of four process variables on moulding rejection rate were investigated: temperature, process pressure, material condition and monomer:polymer ratio.

(a) Effect of Changing Process Temperature

(i) Surface imperfections

At a fixed pressure of 4.5 tons, material condition time of 40 minutes and monomer:polymer ratio of 1:2.7, it was found that as process temperature is increased the melt has greater flow properties and rejection rate begins to fall at temperatures greater than 135°C. Below 135°C the teeth have porosity and contraction marks. At these temperatures the material does not have sufficient flow properties to fill the cavity and maintain a back pressure to overcome the polymerisation shrinkage and quenching residual stresses which will be relieved by formation of bubbles and sink marks[45]. As a consequence of the mould design (Appendix 3), the surface of the tooth will cool first and the back of the tooth last. Thus, if any contraction occurs at the surface, due to either polymerisation or quenching residual stresses, the material in the transfer pot should compensate for the contraction by flowing into the cavity. If the temperature is too low

the material will not be able to flow and compensate for the contractions and the reject rate will be higher. The propensity for the material to form contraction marks may also be increased by a lower temperature because the time of cooling from the maximum temperature to the Tg of the material is lower. This affords the molecules less time to lose the residual stress, so the material will possess greater residual stresses [50].

The reject rate falls to a minimum at a temperature of 175°C (1.25%, Standard deviation (SD) of 0.422). At this temperature the material has sufficient flow properties to compensate for any contractions. The time available for the temperature to fall from the maximum melt temperature to the Tg of the system is also longer and thus allows greater residual stress relief. Reject rate increased when the temperature was increased to 185°C (3.125%, SD of 0.707). Statistical analysis by Student's t-test showed there was no significant difference between the two means. Clearly from a commercial viewpoint it is more beneficial to mould at the lowest temperature thus reducing operating costs.

(ii) Internal porosity

No internal porosity was detected in any of the teeth produced at all of the temperatures studied. The absence of internal or gaseous porosity may be attributed to two factors. As the cavity pressure is greater than atmospheric pressure the boiling point of the MMA will be elevated.[20] The elevation in boiling point will afford an increased time to convert the volatile monomer to a less volatile polymer.

The second factor is that there is a heat gradient across the mould. The mould will be cooler in the middle than at the face of the cavity. Therefore as the monomer boils it will travel away from the tooth towards the transfer pot, thus leaving the tooth free from internal porosity.

(b) Moulding Pressure

(i) Surface imperfections

Results showed that there was no significant difference between the defect rates when the moulding press pressure was greater or equal to four tons, but there was a highly significant increase in defect rate when the pressure was lowered to 3.5 tons. This was because the pressure applied was insufficient to force enough material into the mould under the given moulding parameters. Above 4.5 tons there was no significant difference in rejection rate. The major fault was a contraction mark on the back of the tooth. As the pressure was increased the flash thickness increased. At 6.0 tons this flash thickness was at an unacceptably high value which made the teeth more difficult to finish.

(ii) Internal porosity

None of the teeth produced had internal porosity.

(c) Material Condition

(i) Surface imperfections

Rheological measurements showed that the viscoelastic characteristics of the dough changed with time. The dough's propensity for viscous flow reduced with time and its degree of elasticity increased. If the material is presented to the mould in a state with a high viscous component to its

flow then the material will leak from the mould giving a lack of pressure in the cavity resulting in a defective moulding through surface porosity or sink marks.

If the dough is allowed to mature too much it has a greater elasticity and higher viscosity, ie less viscous flow. The rejection rate will increase because the pressure will not be great enough to create sufficient flow of the material. However, results showed that a process window exists for material condition. The material condition is dependent on the time allowed for monomer:polymer interaction and so for convenience the condition is labelled in terms of time. The process window was found to be between 40 minutes and 90 minutes interaction time at 25°C. Above and below these times there was a significant increase in rejection rate through surface imperfections.

(ii) Internal Porosity

No internal porosity was found in any of the mouldings.

(d) Monomer:Polymer ratio

(i) Surface imperfections

Increasing the monomer content increases the doughing time of the material. Therefore the 1:2.3 ratio will have greater viscous flow at a given time compared to a ratio which has more polymer eg 1:2.7. Both mixes have process windows with respect to material condition but the wetter mix is further along the time axis. For example the process window for 1:2.7 mix is from 40 minutes to 90 minutes after mixing, for a 1:2.3 mix this is from 50

minutes for 120 minutes. The moulder must be aware of monomer:polymer relationship if the reject rate is to be minimised.

(ii) Internal porosity

No internal porosity was found in any of the mouldings.

2.3.5 TRANSFER MOULDED TEETH REJECT RATE DUE TO FAILURE TO COMPLY WITH SPECIFICATIONS SET IN BS3990 1980, ACRYLIC RESIN TEETH

All teeth produced with the moulding conditions described in this chapter passed all the tests specified in BS3990 except for the test for crazing, blushing and distortion; all teeth failed this test. However, experiments indicated that the degree of crazing appeared to increase with increasing process pressure and material conditioning time. Moulding temperature also affected the propensity to craze. Below 155 °C the teeth produced crazed more than those processed at higher temperatures. These observations can be explained in terms of residual stresses arising from molecular orientation and quenching.

As the molecules are pushed from the transfer pot through the die they are orientated during the elongational and shear flow of the dough. If the pressure is increased more material is pushed through the die at a higher viscosity because the material temperature has not risen to provide a melt of lower viscosity. If the pressure has been increased the molecules will also find it more difficult to relax because the increased pressure may maintain the orientated structure by restricting movement, ie forcing the molecules into a specific position. Therefore, formulations processed under a lower pressure will possess less residual stress because the molecules will not

be so highly orientated and they will have greater opportunity to relax in the cavity. Similarly, as condition time is increased the material becomes more elastic and increases in viscosity and will therefore have less tendency to deform and flow. Therefore the molecules will be forced to align in a specific fashion as they flow through the die. This will create orientation which, if it is frozen in during moulding, will result in crazing when the molecules relax due to an increase in free volume, created by water or monomer during the testing regime. Increased temperature reduces the propensity of the material to craze because it allows easier flow through the die by reducing melt viscosity, and by increasing the time allowed for the molecules to relax before they are 'frozen' into position below Tg. Despite using the lowest moulding pressure, minimum conditioning time and maximum temperature in the process window to give the lowest reject rate, the teeth still failed the crazing test. This crazing could be eliminated by increasing the crosslinking of the system [50,53] thus denying the molecules the chance to relax by restricting their movement. This was achieved by increasing the cross-linking agent concentration from 6% to 26% (V/V) of the liquid component. Therefore, the concentration of crosslinking agent required to eliminate crazing from transfer moulded teeth is less than that required to eliminate crazing from pseudo-compression moulded teeth, despite the fact that the latter process is a lower shear rate process and should induce less residual stress [51]. This fact emphasises the important role played by temperature, pressure and material condition in reducing the quantity of residual stresses present in a moulding.

2.4 CONCLUSIONS

2.4.1 PSEUDO COMPRESSION MOULDING

(a) The rate of rejection at moulding due to surface imperfections was unacceptably high and variable. Variability is attributed to entrapped air in the material and possible non-homogeneity of the material mix.

(b) External porosity and sink marks are caused by residual stress relaxation. These residual stresses are induced by configurational volume changes as the monomer is cured to polymer. In a perfect moulding there is sufficient pressure to allow flow of excess material to compensate for any contractions. Residual stresses are also created by cooling the system too rapidly before the molecules have an opportunity to relax.

(c) Internal porosity is a phenomenon induced by the boiling of MMA. Careful control of heating allows the conversion of the monomer to a polymeric material before its boiling point is reached and so no internal porosity is observed. A platen temperature of 115±2 °C was found to eliminate internal porosity in all mouldings.

(d) There was no compliance to BS3990 (1980) Acrylic resin teeth because all teeth failed the crazing test. This signified that there are unrelaxed residual stresses in the moulding. As temperature or pressure could not be altered without detrimentally affecting the moulding reject rate, the crosslinking agent concentration was increased to 40%. Increasing the crosslinking in the moulded structure decreases the propensity of the molecule to flow and so reduces the ability to craze.

2.4.2 NEW TRANSFER MOULD DESIGN

(a) Material Usage

A modified transfer mould transfer pot reduced material usage by 50%.

(b) Cavity Edges

Cavity edges on the traditional mould did not fit properly when the two halves of the mould were brought together. This poor fit allowed material to leak from the cavity affording a reduction in pressure attained in the cavity and a thick flash. The fall in pressure created a greater defect rate. Improvement of the fit and surface finish of the cavity edges reduces the propensity of the material to leak from the mould. This measurably reduces the incidence of rejection but further optimisation of the moulding system is required to reduce rejection to a minimum level.

2.4.3 TRANSFER MOULDING

(a) The Rate of Rejection at Moulding Due to Surface Imperfections

Control of the rheological properties of the dough is a crucial factor in obtaining a perfect moulding. The rheological properties of the material during moulding are a function of: press temperature, pressure, dough condition and monomer:polymer ratio. Optimisation of these variables affords an average moulding reject rate of 1.25%. These conditions allow sufficient material flow and material pressure to compensate for polymerisation shrinkage.

(b) Internal Porosity

Despite using high temperatures (up to 185°C) no internal porosity was observed in any teeth. The absence of any internal or gaseous porosity is attributed to two reasons. Firstly, pressure is applied directly to the material in the cavity and, therefore, if the pressure is increased the boiling points of the liquid present will increase. It is assumed that due to the pressure rise the boiling point of the MMA is increased and that the temperature of the mould does not reach this temperature before all of the monomer is converted to a less volatile substance. The second reason is that there is a negative temperature gradient from the face of the cavity to the transfer pot. Thus any monomer vapour will travel towards the transfer pot via the sprew, leaving the tooth solid.

(c) Compliance to BS3990 (1980)

All teeth produced passed all tests in BS3990 except for resistance to crazing, blushing and distortion. Increasing the crosslinking agent concentration to 25% results in craze-free mouldings. This low concentration, compared to 40% required for pseudo-compression moulding, emphasises the important role played by mould pressure, temperature and material condition in the process of residual stress relaxation.

2.4.4 COMMERCIAL COMPARISON OF PSEUDO-COMPRESSION AND TRANSFER MOULDED TEETH

	Pseudo-Compression Moulded teeth	Transfer Moulded teeth
Defect rate (rounded up)	19%	2%
Number of acceptable teeth per 100	81	98
Material Costs (per 100 teeth)	£1.02	£1.53
Labour Costs (per 100 teeth)	£1.56	£1.56
Overheads (per 100 teeth)	£1.90	£1.90
Total Costs per 100 teeth	£4.48	£4.99
Cost of production for acceptable teeth	£4.48/81 5.5p per tooth	£4.99/98 5.1p per tooth

The cost saving per tooth if the transfer method is adopted is 0.4 pence per tooth, despite having 50% greater material costs. This represents a saving of £4,000 per 1 million teeth made. Therefore the transfer method is more commercially feasible.

Chapter 3: STUDY OF THE EFFECTS OF SEVEN PROCESS VARIABLES ON THE MECHANICAL PROPERTIES OF POLYMER SYSTEMS PRODUCED BY THE TRANSFER METHOD

3.1 INTRODUCTION

3.1.1 PROCESS VARIABLES

It has been established, (Chapter 2), that in moulding artificial teeth by the transfer moulding method, using the process parameters listed below, the rate of rejection is 1.25%. However, there is no evidence to suggest that these parameters yield mouldings which possess optimum mechanical properties. It was, therefore, decided to investigate the influence of process variables on the mechanical properties of the transfer moulded teeth, and thus, identify those process conditions which afforded teeth with superior mechanical properties.

Benzoyl peroxide	0.5% of polymer weight
MMA/PMMA	1:2.7
EGDMA	25% of liquid
Mixing time	2 mins
Material condition time	40 mins at 25°C
Process temperature	175°C
Process pressure	4.5 tons
Time cycle	4 mins heating, 4 mins cooling

Optimum Process Parameters for Transfer Moulded Teeth

Seven process variables were chosen for the investigation:

process temperature;
process pressure;
material condition time;
EGDMA concentration;
(monomer/polymer) ratio;
benzoyl peroxide concentration; and
the concentration of (BisGMA/Tetrahydrofurfuryl methacrylate) comonomer system.

The latter was added as it has been claimed that this comonomer system improves the mechanical properties of polymeric artificial teeth. When polymerised the BisGMA monomer (see Section 7.1.1) which was developed by Bowen[55], has improved strength and stiffness when compared to PMMA due to the incorporation of aromatic groups in the backbone. Braden[12] observed that the addition of 3% - 15% by weight of a heterocyclyl-substituted C_1 - C_4 alkyl methacrylate, such as tetrahydrofurfuryl methacrylate, to BisGMA enhanced the properties of the derived resin. It is believed that heterocyclic methacrylates improve the strength and stiffness of the polymer by reducing the free volume between polymer chains and, hence, restrict molecular movement - ie they act as anti-plasticisers.[12]

The main effect and two-way interaction effects of the above variables on the mechanical properties of the polymers produced were studied. For example, the effect of benzoyl peroxide concentration on tensile strength, or the interaction effect of benzoyl peroxide and process temperature on tensile strength were examined. To determine these effects and establish if they were statistically significant, a factorial replicate experiment was designed.

3.1.2 STATISTICAL DESIGN OF A FACTORIAL EXPERIMENT

Statistical design in process management is employed to derive the maximum amount of information pertaining to the process system from the minimum amount of data. In this particular case the objective was to reduce the number of observations to a manageable quantity whilst not sacrificing the ability to retrieve information about the main and two way interaction effects of the variables on the mechanical properties

of the polymers produced.

Clearly, with seven process variables the number of permutations of these variables at varying degrees of concentration is enormous. Even studying each variable at two levels, one high and one low, to estimate the effects and interactions would require 128 treatment combinations. This experiment is called a 2^7 factorial design[56]. This design yields all of the main and interaction effects. However, some of the interactions, especially those involving a large majority of the variables, are likely to be statistically insignificant. Thus, it would be more time and cost effective to reduce the number of observations to a number which yields all the main effects and the majority of the most significant interactions. The 128 permutations are arranged in four predetermined blocks. The permutations are arranged in the blocks to allow the determination of all the single and two way effects. A quarter replicate of the experiment is achieved by randomly selecting one of the four blocks. Thus, the experiment requires only 32 observations.

Those variables which are found to have the most significant effect on the studied mechanical property of the polymer are then investigated in greater detail. In short, the factorial design is used as a primary screening technique.

3.1.3 PROPERTIES EVALUATED

For all formulations produced, the following parameters were measured:

1. Tensile strength.
2. Young's Modulus.
3. Surface hardness.
4. Storage modulus, E', (1 Hz) at 37, and 158°C.
5. Damping factor, Tan δ (1 Hz) at 37°C.
6. Temperatures for the α relaxation.
7. Gel fraction content.

Determination of the seven properties allowed possible structure-property relationships to be elucidated. Such relationships may explain why certain formulations may be superior to others, highlighting the contribution of variables to the magnitude of a physical property, and thus, the performance of the polymer produced.

3.2 EXPERIMENTAL

3.2.1 PROCESS FORMULATIONS

The 128 permutations, or treatments, of the formulations were determined and listed into four columns of 32. A coin was tossed twice and the combination of heads and, or, tails decided which 32 treatment would be studied. This was found to be column 3. The letter in each treatment represents a variable, if a letter is listed this means the variable is at its high level in the treatment. If a letter is not mentioned in a treatment, it is in its low level in the treatment.

Variable	Symbol	High level	Low level
Process pressure	a	6.5 tons	4.5 tons
Material condition time	b	100 mins	40 mins
Process temperature	C	175°C	145°C
EGDMA	d	20% of liquid	6% of liquid
BisGMA/THFMA	e	20% of liquid	0% of liquid
Monomer/polymer ratio	f	1/2.3	1/2.7
Benzoyl peroxide	g	0.72% wt of dough	0.36% wt of dough

For example, treatment 1 is C, that is a formulation of a to g where only C is at its high level, the rest are at their low levels. All 128 treatments are listed on the next page.

COL 1	COL 2	COL 3	COL 4
1	a	c	f
ab	b	abc	afb
bef	abef	cbef	be
aef	ef	caef	ae
de	ade	cde	def
abde	bde	abcde	abdef
bdf	abdf	bcdf	bd
adf	df	acdf	ad
fg	afg	cfg	g
abfg	bfg	abcfg	abg
beg	abeg	cbeg	fbeg
aeg	eg	aecg	faeg
fgde	afgde	cfgde	gde
abdefg	bdefg	cabdefg	abdeg
bdg	abdg	cbdg	bdgf
adg	dg	cadg	adgf
cd	acd	d	cdf
abcd	bcd	abd	abcdf
cabef	acdbef	dbef	cdbe
cdaef	cdef	daef	cdae
ce	ace	e	cef
abce	ce	abe	acef
cbf	acbf	bf	cb
acf	cf	af	ac
cdfg	acdfg	dfg	cdg
abfcd	bcdf	abfgd	abcd
begcd	abegcd	begd	begcdf
aegcd	egcd	aegd	aegcdf
fgec	afgec	fge	gec
abefgc	befgc	abefg	abegc
bgc	abgc	bg	bgcf
agc	gc	ag	agcf

128 Possible Treatment Combinations of the Seven Variables at Two Levels

3.2.2 SAMPLE PREPARATION

Two types of test pieces were required on which to perform all of mechanical tests - a dumbell and a solid rectangular box. It was imperative that the samples were prepared under the same moulding conditions as teeth, and so a transfer mould was designed to produce the required specimens, (Figure 13). Maintaining a similarity between the methods of moulding of the test pieces and the teeth ensured that any anistropic effects during moulding of teeth would also be present in the test pieces[23]. The surfaces of the mould were highly polished to give a glass like finish on the test pieces.

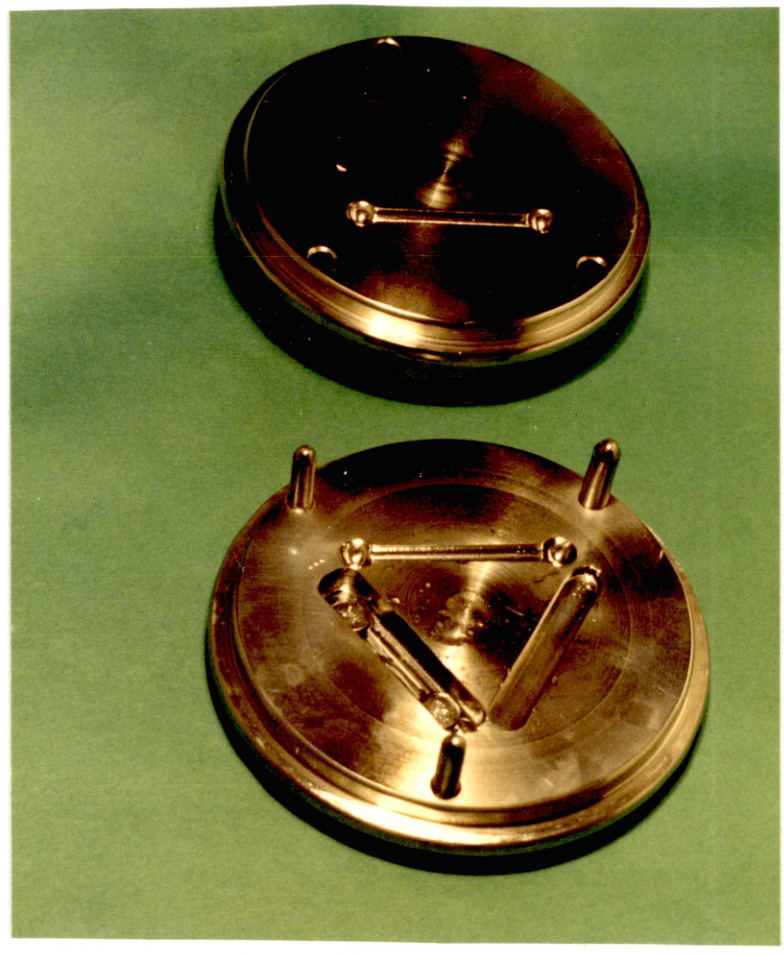


Figure 13 Transfer Mould for Production of Test Pieces

After moulding a test piece, any flashed material was removed and all surfaces were smoothed using emery paper (400 grade to 1200 grade). Any sample which had a surface flaw or inclusion was rejected.

3.2.3 TENSILE STRENGTH

Method

The tensile strength was determined for each formulation using the dumbell moulding (33 mm gauge length, 4 mm diameter) and an Instron*. The dumbell was held in the Instron using Hansfield Number 12 grips. The Instron was programmed to apply the strain at a rate of 1×10^{-4} ms^{-1}. The strain was applied until the material failed by fracturing; this load was recorded. This was repeated five times per formulation.

$$\text{Tensile strength} = \frac{\text{Load at fracture}}{\text{Cross-sectional area at fracture}} \qquad (17)$$

The main effects and two way interactions were calculated and compared with the test statistic for a level of significance of 1% and 5% (Appendix 5).

*Instron TTCM. Instron Ltd, High Wycombe, England

Results

	Treatment	Tensile Strength (Kg cm^{-2}) mean	Standard deviation
1.	c	868	14.31
2.	abc	877	13.9
3.	cbef	874	16.04
4.	caef	918	19.35
5.	cde	954	5.2
6.	abcde	957	15.59
7.	bcdf	908	25.6
8.	acdf	821	12.9
9.	cfg	942	12.2
10.	abcfg	917	37.3
11.	cbeg	890	13.4
12.	aecg	904	14
13.	cfgde	788	20.9
14.	cabdefg	765	20.94
15.	cbdg	849	21.37
16.	cadg	869	13.62
17.	d	916	4.9
18.	abd	818	17.8
19.	bdef	835	7
20.	adef	807	8.5
21.	e	887	13.0
22.	abe	857	40.16
23.	bf	814	15.5
24.	af	883	12.7
25.	dfg	879	9.9
26.	abdfg	837	10.9
27.	begd	865	16.8
28.	aegd	830	10.8
29.	fge	839	26.25
30.	abefg	880	7.15
31.	bg	927	19.7
32.	ag	893	11.9

Statistical Analysis

Using the tests of significance outlined in Appendix 5, the following main effects and interactions were found to significantly affect tensile strength:

(a) BisGMA/THFMA concentration - benzoyl peroxide concentration. ($p \leq 0.05$)

(b) EGDMA - benzoyl peroxide concentration. ($p \leq 0.01$)

Both interactions significantly decreased the tensile strength.

3.2.4 TENSILE MODULUS

Method

The tensile modulus was determined using the same procedure as in 3.2.3 except that the maximum load applied to the test specimen was 65 kg. The modulus is given by:

$$E = \frac{d\sigma}{d\varepsilon} \qquad (18)$$

where, E = Young's modulus
σ = stress
ε = strain

and was calculated from the stress-time curve produced by the Instron testing machine, by translating the curve into a stress-deformation curve by multiplying by a conversion factor to transform time to deformation. Modulus was calculated by measuring the gradient of the linear part of the load versus deformation curve.

The main effects and two way interaction effects were tested for significance at the 1% and 5% level.

Results

Static Young's Modulus

Treatment	Modulus	Standard Deviation
1	2.276	0.053
2	2.750	0.068
3	2.21	0.118
4	2.21	0.068
5	2.242	0.026
6	2.2375	0.11
7	2.214	0.043
8	2.200	0.06
9	2.168	0.05
10	2.234	0.054
11	2.26	0.01
12	2.214	0.068
13	2.278	0.014
14	2.265	0.017
15	2.272	0.017
16	2.196	0.108
17	2.130	0.054
18	2.120	0.001
19	2.140	0
20	2.160	0.147
21	2.000	0.05o
22	2.050	0.043
23	2.150	0.068
24	2.150	0.068
25	2.148	0.054
26	2.165	0.043
27	2.250	0.016
28	2.280	0.016
29	2.270	0
30	2.250	0.147
31	2.27	0.137
32	2.34	0.143

Statistical Analysis

The following effects and interactions significantly affected the modulus value:

(a) Temperature increases the modulus. ($p \leq 0.01$)

(b) Bis GMA/THFMA concentration - monomer/polymer ratio increases the modulus. ($p \leq 0.05$)

(c) BisGMA/THFMA concentration - EGDMA increases the modulus. ($p \leq 0.05$)

(d) BisGMA/THFMA concentration - benzoyl peroxide concentration increases the modulus. ($p \leq 0.01$).

(e) Temperature - benzoyl peroxide concentration decreases the modulus. ($p \leq 0.01$)

3.2.5 SURFACE HARDNESS

Method

The surface hardness of each treatment was determined using a Shore D durometer. This instrument measures hardness in terms of the ability of the material to resist penetration by a steel pin. The resistance to penetration is measured by a calibrated spring. A force applied to the durometer is transmitted to the penetrator via the spring. If there is resistance to penetration, the spring will compress and the greater the compression the harder the material. The degree of compression is measured by a dial on the face of the instrument. The dial has a scale of 0 to 100. The hardest material will have a value of 100.

The durometer was placed on top of the test piece (50 mm x 7.9 mm x 2 mm) on a flat surface and forced downwards until it was flat against the sample. The durometer was kept

in this position for 30 seconds to allow for any relaxation to occur, and then a reading was recorded. This procedure was repeated five time on each surface for each treatment.

The main effects and two way interactions were tested for significance of 1% and 5% level, as outlined in Appendix 5.

Results

Treatment	Surface hardness	Standard deviation
1	88	0.52
2	87	0.74
3	88	0.70
4	87	0.97
5	87	0.74
6	87	0.67
7	86	0.92
8	86	0.70
9	87	0.63
10	87	0.85
11	86	0.48
12	87	0.74
13	87	0.74
14	87	0.74
15	86	1.95
16	86	0.53
17	86	0.67
18	85	0.67
19	87	0.47
20	87	0.79
21	87	0.67
22	85	0.52
23	85	0.67
24	84	1.50
25	87	0.47
26	87	0.52
27	85	0.74
28	85	0.84
29	86	0
30	86	0.42
31	86	0.57
32	86	0.32

Statistical Analysis

All of the main effect and two way interaction effects were calculated and compared with a limiting value in accordance to the method described in Appendix 5.

None of the effects or interaction effects were greater than the limiting value, and so none of the variables had a significant effect on Surface hardness, at the two levels studied.

3.2.6 VISCOELASTIC PROPERTIES

Method

The viscoelastic properties include the storage modulus, (E'), the damping factor, (tanδ), and the alpha - and beta - relaxation temperature.

All of these properties were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyser* (DMTA). A sample specimen (50 mm x 7.9 mm x 2 mm) was clamped into a dual cantilever frame. For temperatures between -50°C and +100°C, a 14 cm frame was used, but for temperatures between 100°C and 160°C, a 7 cm frame was used. The longer frame was used for the lower temperature because at these temperatures the material is stiffer; so in order to give a better displacement signal a longer gauge length is used. Specimen measurements and gauge lengths afford the calculation of the geometry constraint.

Each specimen was analysed from -50°C: to +160°C, heating at a rate of 1°C min^{-1}, at frequencies of 0.33 Hz, 1 Hz, 3 Hz, 10 Hz and 30 Hz. The analyser unit in the instrument compares the stress and strain signals. The strain is resolved into its

* Polymer Laboratories, Loughborough, England

storage and loss components. The instrument then calculates the storage modulus, the loss modulus, and the damping factor, at the given frequencies across the temperature sweep of -50°C to 160°C. The computer then plots the storage modulus, the loss modulus and the damping factors against temperature at given frequencies. The following data were then recorded: $E_{158°C}$, $E_{37°C}$, $\tan\delta_{37°C}$, and $T\alpha$.

The effects and interactions of the variables on these viscoelastic properties were evaluated and tested for significance at 1% and 5% level.

Results

Treatment	Tα	E'(158 °C) (MPa)	Tanδ37 °C	E'(27°C) (GPa)
1	124	2.864	0.0787	2.355
2	123	2.825	0.0767	2.369
3	129	4.943	0.0667	2.729
4	128	4.797	0.0713	2.138
5	127	3.724	0.0723	2.211
6	128	3.443	0.0736	2.267
7	126	4.385	0.0750	2.382
8	128	3.710	0.0803	2.291
9	125	2.850	0.0793	2.046
10	126	3.048	0.0796	2.153
11	124	2.460	0.0717	2.455
12	123	2.495	0.0771	2.158
13	126	5.333	0.0696	2.393
14	127	5.058	0.0745	2.399
15	125	2.990	0.0792	2.213
16	125	2.979	0.0722	2.371
17	127	3.013	0.0850	1.951
18	126	3.256	0.0849	2.110
19	126	2.860	0.0806	2.178
20	127	2.938	0.0810	2.280
21	126	3.124	0.0836	2.133
22	128	3.624	0.0852	2.163
23	124	2.606	0.0875	2.222
24	124	2.610	0.0895	1.816
25	126	2.908	0.0852	1.982
26	125	3.076	0.0847	1.941
27	125	2.09	0.0829	2.048
28	127	2.537	0.0870	1.998
29	126	2.320	0.0880	2.125
30	124	2.000	0.0875	2.048
31	123	2.692	0.0820	2.200
32	122	2.706	0.0815	2.244

Statistical Analysis

T_α(1Hz) was significantly affected by the following at high levels:

(a) Concentration of EGDMA increased T_α ($p \leq 0.01$).

(b) Concentration of BisGMA/THFMA increased T_α ($p \leq 0.01$).

(c) Concentration of benzoyl peroxide decreased T_α ($p \leq 0.01$).

(d) Monomer/polymer ratio and temperature increased T_α ($p \leq 0.01$).

E'(1Hz) at 158 C was significantly affected by the following at high levels:

(a) Concentration of EGDMA increased E'.

(b) Concentration of BisGMA/THFMA increased E'.

(c) Monomer/polymer ratio increased E'.

(d) Temperature increased E'.

(e) Concentration of BisGMA/THFMA and the monomer/polymer ratio increased E'.

(f) Concentration of BisGMA/THFMA and temperature increased E'.

(g) Concentration of EGDMA and temperature increased E'.

(h) Concentration of EGDMA and the benzoyl peroxide concentration increased E'.

(i) Concentration of EGDMA and the monomer/polymer ratio increased E'.

(j) Temperature and the monomer/polymer ratio increased E'.

(k) Concentration of benzoyl peroxide reduced E'.

(All levels of significance $p \leq 0.01$)

Tanδ(1Hz) at 37°C was significantly affected by the following at high levels:

(a) Temperature decreased tan δ ($p \leq 0.01$).

E'(1Hz) at 37°C was significantly affected by the following at high levels:

(a) Temperature increased E'(1Hz) ($p \leq 0.01$).

3.2.7 EVALUATION OF INSOLUBLE GEL CONTENT

Method

The quantity of unsoluble gel present was determined by dissolving the soluble, uncrosslinked polymer in tetrahydrofuran. A known quantity of granulated polymerised material was added to a Soxhlet thimble which was then placed in the apparatus and the tetrahydrofuran was refluxed for twenty four hours. After this period the undissolved solids were dried *in vacuo* at 80 C for twenty four hours. The dried material was then weighed. Any effects or interaction effects were calculated and tested for significance of 1% and 5% levels (Appendix 5).

Results

Treatment	Percentage weight of material that extracted by Tetrahydrofuran (sol content)
1	48.600
2	51.651
3	54.580
4	55.160
5	61.100
6	59.002
7	52.001
8	55.202
9	49.400
10	52.290
11	54.680
12	56.942
13	49.861
14	56.234
15	60.500
16	61.240
17	63.241
18	61.650
19	56.240
20	53.351
21	66.730
22	61.651
23	54.040
24	58.870
25	51.151
26	48.805
27	49.400
28	52.304
29	65.451
30	61.590
31	63.100
32	60.400

Statistical Analysis

Statistical analysis showed that the sol/gel ratio of the formulation was not significantly affected by any of the process variables at their two levels.

3.3 DISCUSSION

3.3.1 TENSILE STRENGTH

The tensile strength of the resin was significantly reduced by two two-way interactions: *BisGMA/THFMA - benzoyl peroxide concentration* ($P \leq 0.05$) and *EGDMA - benzoyl peroxide concentration* ($P \leq 0.01$). EGDMA and BisGMA are both dimethacrylates and will therefore be able to crosslink PMMA molecules [57]. Berry [27] has reported that introduction of crosslinks into a PMMA system reduces the flaw size by a factor of three, whilst reducing the surface energy by a factor of five. Therefore, by applying equation (19) it is seen that the strength of the polymer is reduced by the introduction of crosslinks.

Assuming plane stress then,

$$\sigma = \left(\frac{2\gamma E}{2\pi C_0}\right)^{\frac{1}{2}} \qquad (19)$$

when, γ = fracture surface energy
C_0 = inherent flaw size
E = Young's modulus

The reduction in tensile strength is perhaps a result of the loss of viscous or plastic processes at the crack tip. Such processes increase the tensile strength by viscous dissipation of the applied force. [59] The viscous processes are reduced due to increased rigidity of the structure created by crosslinking.

Wollff [58] observed that tensile strength of dental PMMA was not significantly affected by crosslinking agent concentration until it was in excess of 25%. The fact that this research showed that a crosslinking agent concentration of 20%, with an initiator concentration of 0.75% reduced tensile strength, may be attributed to the efficiency of the crosslinking reaction at higher temperatures - 145°C rather than 100°C. At higher temperatures the reactive species will have greater energy/

mobility[60,68] and will have a greater opportunity to react with another molecule thus increasing the number of crosslinks. Also, at greater temperatures the resin will have a lower viscosity - ie it will be more mobile. This enhanced mobility may be conducive to enhanced conversion the monomers[61].

3.3.2 YOUNG'S MODULUS

The Young's modulus was significantly increased by:

Temperature, ($p \leq 0.01$).

BisGMA/THFMA-benzoyl peroxide, ($p \leq 0.05$).

BisGMA/THFMA-(monomer/polymer) ratio, ($p \leq 0.01$).

BisGMA/THFMA-EGDMA, ($p \leq 0.05$).

Temperature-benzoyl peroxide concentration, ($p \leq 0.01$).

Increasing the *temperature* of the reaction increases the kinetic energy of the reacting species, and therefore, increases their propensity to react[60]. This, theoretically, should reduce the number of residual methacrylate groups in the network. The residual groups are present in the form of low molecular weight species and pendant groups[62]. They may behave as plasticisers in the network[63], increasing the free volume in the polymer, and in doing so, reducing the molecules of the polymer. Reducing the quantity of the residual methacrylate groups therefore will increase the modulus of the network. High levels of *BisGMA/THFMA* and *benzoyl peroxide* increased the modulus significantly. The increased initiator level will increase the number of radicals present in the matrix. Therefore, there will be a greater probability of reaction of the BisGMA. Incorporation of BisGMA increases the polymer rigidity because of the aromatic rings[39] in its backbone and its ability to form crosslinks between linear polymer molecules.

It has been reported[61] that diluent monomers, such as EGDMA, increase the mobility of the BisGMA molecules, which induces a greater degree of conversion, thus enhancing the mechanical properties of the polymerised material. This theory would account for the observation that increasing the *BisGMA/THFMA* concentration and *monomer/polymer* ratio to their highest levels increased the modulus of the resin produced. The lower viscosity comonomer system increased the mobility of the BisGMA, allowing for a greater degree of conversion. Addition of 20% of both *BisGMA/THFMA* and *EGDMA* severely slowed the doughing process between the polymer and the comonomer. Therefore, at any particular time, the dough with high levels of these variables had a lower viscosity than doughs without both of them in high levels. Thus, once again the BisGMA would have had a greater mobility; this may have lead to greater conversion of the BisGMA, resulting in an improved modulus.

The only two-way interaction that significantly reduced the modulus was that of *temperature* and *benzoyl peroxide*. This observation may be explained from steady state kinetic examination of free radical addition polymerisation[60]. There are three steps in such polymerisations: initiation, propagation and termination. In steady state kinetics, the rate of initiation is assumed to be equal to the rate of termination. The overal rate of polymerisation is given by equation (20).

$$V_p = k_p \{fk_d [I] / k_t\}^{\frac{1}{2}} [M] \qquad (20)$$

where V_p = Rate of polymerisation.

k_p = Rate constant of propogation.

k_d = Rate constant of decomposition of monomer.

k_t = Rate constant for termination.

f = Radical efficiency factor.

M = Monomer concentration.

But, the kinetic chain length, j, which is a measure of the average number of monomer molecules per polymer molecule chain is given by equation (21).

$$j = \frac{k^2_p[M]^2}{2k_t V_p} \qquad (21)$$

Thus, j is inversely proportional to V_p. Given that V_p is increased by temperature and radical concentration, then the chain length of the polymer must decrease as both temperature and radical concentration increase.

This reduction in chain length increases the number of the low molecular weight species, thus reducing the average molecular weight and so the modulus will be reduced.

3.3.3 SURFACE HARDNESS

Wollff [58] concluded that the increased crosslinking agent concentration did not significantly change the surface hardness of heat cured denture base materials. This research has found that none of the seven process variables studied, significantly affected the hardness of the polymers produced. It has been reported that there is a significant correlation between the surface hardness of a polymer and the quantity of residual double bonds in the material [64]. Thus, none of the variables in the present study significantly affect the degree of

conversion of the methacrylic double bonds. However, it must be stressed that the degree of conversion is not the same as degree of polymerisation. The degree of conversion is that quantity of the sp^2 carbon atoms that have been converted to sp^3 carbon atoms joined by single bonds. The degree of polymerisation is the number of monomer molecules per polymer chain and so refers to the kinetic chain length[60].

Therefore, although the hardness of the materials may be identical, their networks can be completely different. This is exemplified in the present work. Despite having markedly differing tensile strengths and viscoelastic properties due to significantly dissimilar network structures, all of the materials had similar hardness. Finally, it may also be argued that this method of determining surface hardness does not have the required sensitivity to detect the subtle differences in network structure, although previous researchers believe it does.[64]

3.3.4 VISCOELASTIC PROPERTIES

(a) The Alpha Relaxation

The alpha (α) relaxation is associated with the glass transition temperature of the polymer at a given frequency[14]. It is generally accepted that this relaxation is the micro-Brownian motion of molecular segments. At this temperature and frequency, segments of the chain may move, forming new conformational arrangements of the backbone of the polymer[37]. To allow micro-Brownian motion, the segments must have a space to move into; therefore, the relaxation is dependent on the free volume in the polymer

network[33]. At Tg there is sufficient free volume into which the molecule segments can move. Below Tg there is not enough free volume for micro-Brownian motion and so only rotational and vibrational motion may take place. The latter movements are associated with the glassy state and the former with the rubbery state. Therefore, any factor which can reduce the temperature at which the free volume required for micro-Brownian motion is present will lower the Tg. Similarly, if a factor increases the propensity of the molecules to move into a smaller free volume, for example chain flexibility, the Tg will also be decreased. The α relaxation, measured at a frequency of 1 Hz, was found to be significantly ($p \leq 0.01$) affected by four process variables: *Crosslinking agent concentration; BisGMA/THFMA concentration; the initiator concentration;* and *the interaction between temperature and the monomer/polymer ratio.* *EGDMA* and *BisGMA/THFMA* at their high levels both significantly increase the Tg of the tooth polymers. Both of these monomers are dimethacrylates and will, therefore, have five possible mechanisms of polymerisation reaction[57]. (Figure 14).

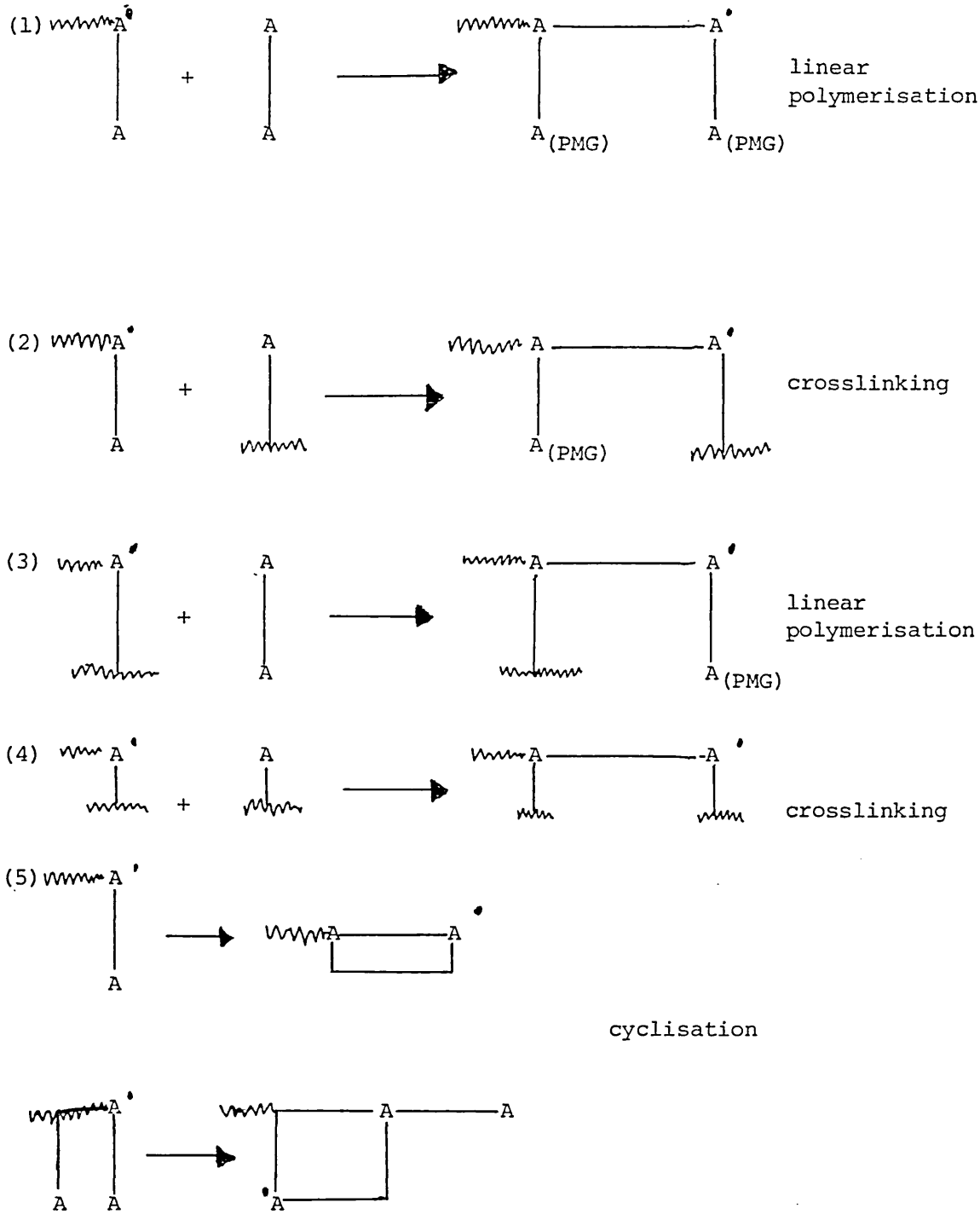


Figure 14 Polymerisation of Dimethcrylates

Key A - A = Dimethacrylate

~~~= Polymer chain

• = Free radical

PMG = Pendant methacrylate groups
~~~

The linear polymerisation steps would increase the molecular weight of the system thus raising the Tg [37]. Crosslinking the network reduces the ease of movement of the polymer molecules by creating large, 3-dimensional networks. Thus, a greater free volume needs to be present to allow movement. This has the effect of shifting the Tg to a higher temperature [33,37].

Cyclisation of the pendant methacrylate group affords a bulkier side group, which increases the steric bulk of the molecule and, thus, may reduce its ability to move. Once again, the effect is to increase the Tg. However, due to the possible difference in volumes between the cyclic and linear pendant methacrylate groups, one may assume this to be a secondary effect.

A shoulder peak to the main α relaxation is observed to varying degrees in all spectra (Figure 15). The shoulder occurs between 70°C and 80°C and moves in sympathy with the T_α of each treatment.

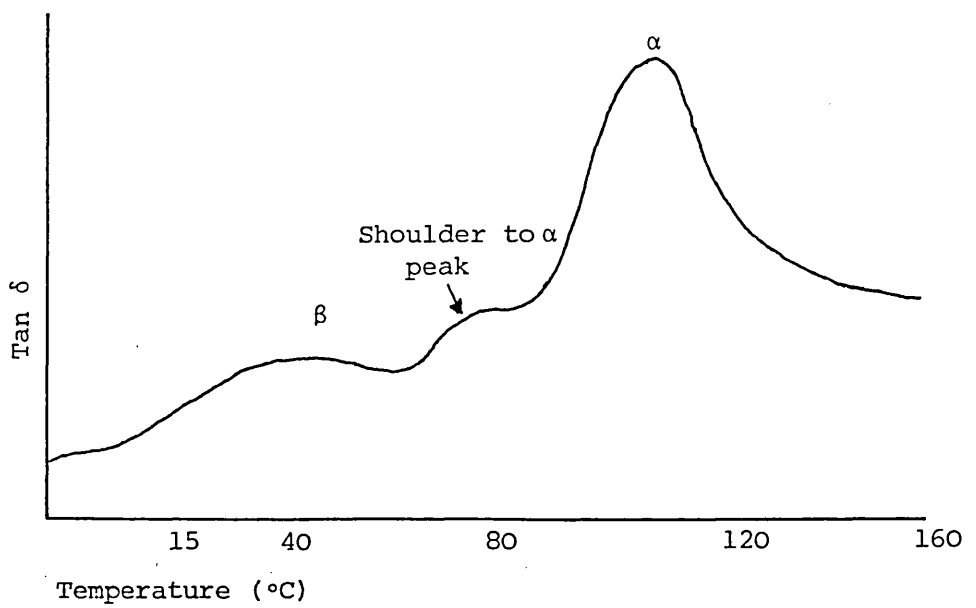


Figure 15 Typical Spectra of Tooth Formulation

It is proposed that this shoulder is the α relaxation of polymer chains which possess pendant methacrylate groups. In the example of PMMA and poly-(n-propyl methacrylate), the longer side chain of the latter induces the polymer to have an α relaxation below that of the PMMA[65]. The same principle may be applied to PMMA and the polymer with a longer pendant methacrylate side chain; the latter having a slightly lower Tg. However, as the relaxations are so close, the polymer with the pendant methacrylate group side chain will appear as a shoulder to the main relaxation. There is no possibility of this 'shoulder' peak being the β relaxation of the PMMA as this relaxation occurs across a broad temperature range at 1 Hz, peaking at 40°C[21]. However, as dental acrylics are heterogeneous systems[5], the shoulder peak and the main peak may be the separate relaxations of the sol phase and the crosslinked gel phase. This phenomenon is observed in phase separated mixtures and depends on the degree of compatability between phases and the degree of mixing. The sol phase would give a lower α relaxation than the crosslinked gel phase, it not being crosslinked[37].

(b) Storage Modulus (E') at 158 C and 1 Hz

In a perfectly elastic body large-scale movement or flow is prevented by the cohesive forces of a diffuse network structure. If the network is broken down, the elasticity of the body is reduced. The value of the storage modulus of a polymer above Tg gives an indication of the extent of the network structure in the polymer

which will primarily depend on the degree of crosslinking and the quantity of low molecular weight molecules present[37]. Generally, the greater the degree of crosslinking, the greater will be the network present and so E' will be large. Low molecular weight molecules and pendant methacrylate groups will increase the free volume present in the system and, so, encourage large-scale flow, thus reducing E'[37].

Ferracane[41] found that a good correlation exists between the degree of conversion in unfilled dental resins and E' above Tg. He also found that the correlation between structure and static modulus at ambient temperatures was not as strong. Ferracane's findings were also observed in this research where it was found that E' was the most sensitive to changes in polymer structure.

Viscoelastic properties are greatly influenced by the structure of the polymer. Polymer chains with less flexible backbones have a reduced ability to flow and move, thus increasing the temperature of the α relaxation[37]. *BisGMA*, due to the presence of two aromatic rings[39], has a relatively rigid backbone. This increases the rigidity of the copolymer chains and, therefore, the chains will not be able to flex and move in free volume. Hence, the Tg will be increased as more free volume is required to allow micro-Brownian movement[37].

Increased polarity will also increase the Tg due to the formation of hydrogen bonding. The hydrogen bonds will increase the resistance to movement[37]. *BisGMA* possesses two hydrophilic alcohol groups which will hydrogen bond with

other polar groups resulting in resistance to micro-Brownian movement.

High levels of both *temperature* and the *monomer/polymer* ratio significantly increased the Tg. It has been reported[66] that when the monomer is crosslinked in the presence of the polymer an interpenetrating network (IPN) is formed. The resulting structure is one in which the polymerised crosslinked monomer is interwoven with the polymer molecules. IPN's are, therefore, more rigid than linear polymers. The increase in Tg may, therefore, result in a larger IPN being formed. This larger network would require greater free volume for micro-Brownian motion. However, to ensure that there is a reduced quantity of pendant methacrylate groups and low molecular weight chains, an increased temperature is necessary. This higher temperature increases the heating rate of the mould, and so improves the efficiency of the polymerisation of the extra monomer molecules in the high monomer/polymer ratio.

As already discussed, (3.3.2), it has been shown that increasing the initiator concentration reduces the molecular weight of a polymer. The molecular weight distribution effects the Tg[38]. As free volume around chain ends is taken to be greater than any other part of the chain because of packing, the larger the proportion of the lower molecular weight fraction the greater the free volume, and the lower Tg. Polymer chains with a molecular weight greater than 1.5×10^5 do not affect the Tg as the concentration of chains ends is negligible.[38]

The following significantly affected the value of the storage modulus measured at 158°C: *Temperature; EGDMA concentration; BisGMA/THFMA concentration:* the *monomer/polymer ratio; high concentration of BisGMA/THFMA* and *monomer/polymer ratio; BisGMA/THFMA* and *temperature; EGDMA* and *temperature; EGDMA* and *monomer/polymer ratio; EGDMA* and *benzoyl peroxide; temperature* and the *monomer/polymer ratio;* and *benzoyl peroxide concentration.*

The effects of BisGMA/THFMA; EGDMA; initiator and temperature and monomer/polymer ratio, on the rigidity of the polymer in terms of crosslink density and molecular weight have already been discussed in Section 3.3.4 (a).

Temperature significantly increased the value of E' above Tg. The temperature may affect the quality of the network in two ways. Increasing the temperature increases the degree of conversion of the methacrylic double bonds[68]- thus reducing the quantity of residual and pendant methacrylate groups. Reduction in these residual and pendant methacrylate groups will decrease the amount of free volume available, restrict flow, and increase E' . Apart from reducing the amount of free volume, conversion of pendant methacrylate may result in increased crosslink density[68]. Increasing the crosslink density would also increase E'.

The *monomer/polymer* ratio was found to significantly increase E'. Koblitz [67] reported that a critical volume fraction of monomer is required to wet all of the polymer

beads in the dough. Incomplete wetting results in a more hetrogeneous system, affording inferior mechanical properties. Thus, a higher monomer/polymer ratio may ensure better wetting and imbibition of the monomer by the polymer beads. Another possible explanation for the observed increase in E' is that the greater amount of monomer present and available to crosslink results in a larger interpenetrating network. The formation of the interpenetrating network yields a more rigid network and so E' would be increased.

The interaction between *temperature* and the *monomer/polymer ratio* significantly increased E'. This observation may be explained by the fact that increased temperature will reduce the residual methacrylate groups, thus reducing the free volume, and increasing the number of crosslinks, thus augmenting the benefits derived from only using a high monomer/polymer ratio.

The storage modulus was also significantly increased by the interaction between *BisGMA/THFMA* and the *monomer/polymer ratio*. As was discussed earlier in Section 3.3.1, a higher diluent concentration improves the degree of conversion of the methacrylic double bonds in BisGMA by improving the mobility of the BisGMA[68]. Improved degree of conversion will afford a tighter network and so E' is increased. As BisGMA is a dimethacrylate and, therefore, a crosslinking agent, increasing the proportion of monomer and BisGMA will afford a proportionally greater crosslinked polymer; thus E' would increase.

The degree of conversion of BisGMA is also increased by increasing the temperature[68] and therefore increasing *BisGMA/THFMA* and *temperature* resulted in a higher value of E. Similarly the interaction between *EGDMA* and *temperature* also raised E'. A possible explanation for this is that by increasing the temperature, the quantity of residual or pendant methacrylate groups was reduced, thus affording a higher degree of crosslinking.

Another method of elevating the degree of conversion of pendant methacrylate groups is to increase the number of reactive sites present for a reaction. High levels of *benzoyl peroxide* and *EGDMA* afforded an increased E' at 158°C. The peroxide may have increased the free radical concentration to a sufficient level in order to improve the probability of conversion of the pendant methacrylate groups, yielding a more crosslinked network.

Finally, the interaction between *EGDMA* and the *monomer/polymer ratio* significantly increased the value of the storage modulus measured at 158°C. As with BisGMA and the monomer/polymer ratio, high levels of EGDMA and monomer/polymer ratio should lead to the formation of a more crosslinked network as the volume fraction of potentially crosslinkable material has been increased.

(c) Storage Modulus (E') and Damping Factor (tanδ) at 37°C and 1 Hz

Both E' and tan δ at 37°C were significantly affected by processing at higher temperatures. High temperature increased the value of E' at 37°C, ie the elasticity of the system at 37°C was increased by processing at 175°C rather than 145°C. The increased E' may be attributed to the higher temperature affording a greater degree of conversion resulting in less lower molecular weight chains and pendant methacrylate groups to plasticise the network[61].

Given that the damping factor, tan δ, is equal to the ratio of the loss modulus to the storage modulus it is not surprising that as temperature significantly elevates the storage modulus it significantly decreases tanδ. The greater the value of tan δ the greater a creep rate a material will have [43]. This is due to the fact that the material will have a larger viscous component and will, therefore, have a greater propensity to flow. By reducing the quantity of lower molecular weight chains and pendant methacrylate groups, the ratio of the viscous and elastic components in the behaviour of the material has been reduced so the material will have a reduced creep rate[42].

3.3.5 SOL/GEL CONTENT

The amount of insoluble gel in a polymer is used as an index of the degree of crosslinking in the material[61]. The crosslinked structure formed during the polymerisation reaction is insoluble in many organic solvents, whereas non-crosslinked material will dissolve.

The average gel content from the thirty two formulations was 44% and statistical analysis showed that none of the variables

significantly affected the sol/gel content.

The average gel content was greater than the expected potential gel content which equals the quantity of monomer present in the dough. The increased gel fraction may be attributed to an interaction between the polymerisable monomer and the prepolymer forming an interpenetrating network[14] . The interpenetrating network (IPN) will be a semi II IPN, as a monomer is being crosslinked in the presence of an uncrosslinked polymer[14] . The IPN structure is a result of the monomer firstly imbibing the prepolymer then snaking between the entanglements of the prepolymer. On polymerisation the monomer forms a 3-D crosslinked network interwoven with prepolymer chains.

Another possible explanation for the increased gel content is the formation of covalent chemical bonds between the uncrosslinked prepolymer and the crosslinked structure by a graft copolymerisation method.[62]

Ruyter and Oysaed[62] have reported that differences in sol/gel ratios in denture base materials are possibly due to initial agent concentration - the greater the amount of crosslinking agent present the greater the content of gel.

The sol/gel ratio was not significantly affected by the process variables. This may be attributed to the sensitivity of the test method.

3.4 CONCLUSIONS

(a) A quarter replicate of a 2^7 factorial design may be used to establish correlations between process variables and the mechanical properties of polymers produced by the process.

(b) The mechanical properties, and therefore, the structure of a polymer, are significantly affected by process variables. Levels of significance were set at 1% and 5%. However, the correlations which are significant at 1% are the strongest, and, hence, the most reliable.

(c) The mechanical properties, and, therefore, the structure, of the tooth polymers produced by a rapid high temperature dough technique are affected by the process variables. Changes in structure may be the direct result of altering the level of a process variable, or due to the interaction effects of two variables.

Tensile strength is significantly decreased by the interaction between high levels of EGDMA and benzoyl peroxide ($p \leq 0.01$) and high levels of BisGMA/THFMA and benzoyl peroxide ($p \leq 0.05$).

Young's Modulus is significantly increased by raising temperature ($p \leq 0.01$). The modulus is also significantly increased by interactions between high levels of the following: BisGMA/THFMA and monomer/polymer ratio ($p \leq 0.05$); BisGMA/THFMA and benzoyl peroxide ($p \leq 0.05$); and BisGMA/THFMA and EGDMA ($p \leq 0.05$). The interaction between temperature and benzoyl peroxide significantly decreased the Young's modulus ($p \leq 0.01$). *Hardness* is not affected by changing the levels of the seven process variables.

The glass transition temperature measured at 1 Hz is affected by changing four of the variables to their higher levels. EGDMA, BisGMA/THFMA, and the monomer/polymer ratio all significantly increase Tg ($p \leq 0.01$), whilst benzoyl peroxide decreases Tg ($p \leq 0.01$).

The Storage Modulus measured at 1 Hz and at 158 °C is significantly affected by a total of eleven effects ($p \leq 0.01$): temperature; EGDMA; BisGMA/THFMA; and the monomer/polymer ratio all increase E' when they are at a high level. Benzoyl peroxide decreases E' when it is at a high level. Additionally, the following two way interactions increase E' significantly: BisGMA/THFMA and monomer/polymer ratio; BisGMA/THFMA and temperature; EGDMA and temperature; EGDMA and benzoyl peroxide concentration; EGDMA and monomer polymer ratio; and temperature and the monomer/polymer ratio.

The damping factor, tan δ, measured at 1 Hz and at 37 °C and the *storage modulus, E', measured at 1 Hz and at 37 °C* are both significantly affected by temperature. *Tan δ* is significantly reduced by temperature whilst *E'* is significantly increased by temperature.

Chapter 4: INVESTIGATION OF THE EFFECTS OF VARYING THE CONCENTRATION OF BISGMA/THFMA AND BENZOYL PEROXIDE ON THE MECHANICAL PROPERTIES OF A POLYMER SYSTEM PRODUCED BY THE TRANSFER MOULDING TECHNIQUE

4.1 INTRODUCTION

It was observed in Chapter 3 that the five variables which had some influence on the strength and stiffness of the polymerised resins were: temperature, EGDMA concentration, BisGMA/THFMA concentration, the monomer/polymer ratio and benzoyl peroxide concentration.

Temperature could not be increased any higher than 175°C because the temperature at which the rate of polymerisation of MMA is equal to the rate of depolymerisation of PMMA is 200°C[60].

It was decided not to investigate the effects of further increasing the EGDMA concentration as this would have a detrimental effect on strength and, possibly, the stiffness if the methacrylate groups were not completely polymerised [58,63].

It was impractical to decrease the monomer/polymer ratio any further for two reasons. First, if the monomer content was increased, the volume shrinkage due to polymerisation of the monomer would also increase. This would cause problems at moulding and, because of the greater volume changes, may create greater residual stresses within the moulding. Secondly, an increased monomer content in the monomer/polymer dough will result in a longer dough time, ie the time taken by the dough to reach the optimum moulding condition will be increased. This would pose major problems in the high volume production of polymeric artificial teeth.

It was shown earlier, (3.3.2), that the BisGMA/THFMA comonomer system improved the stiffness of the polymerised resin. Strength was decreased by high levels of BisGMA/THFMA and benzoyl peroxide. However, this was only significant at

the 5% level, whereas the EGDMA/benzoyl peroxide interaction was significant at the 1% level.

Braden[12] showed that by careful optimisation of the BisGMA/THFMA comonomer and initiator concentration, the strength and stiffness of polymerised resin could be maximised. It was therefore decided to evaluate the effects of altering the BisGMA/THFMA comonomer and the benzoyl peroxide concentrations in a high temperature short-time polymerisation reaction on the mechanical properties of the polymers produced. The formulations were processed with the high levels of temperature, monomer/polymer ratio and EGDMA as stipulated in Chapter 3, in an attempt to achieve the optimum formulation for acrylic resin teeth.

Once again, a factorial design was employed to elucidate the effects and interactions of changing the BisGMA/THFMA and benzoyl peroxide concentrations. On this occasion the experimental design was such that the initiator concentration was studied at three levels and the BisGMA/THFMA concentration at five levels.

The mechanical properties evaluated were:

(a) flexural strength;

(b) Young's modulus;

(c) surface hardness;

(d) viscoelastic properties.

Strength of each resin was determined by measuring flexural strength, rather than tensile strength, because the tensile method often resulted in failure outside the gauge length which required several runs to be repeated. It was also established that, when more brittle materials were being tested, clamping was

difficult and if any shear forces were applied, because the specimen was not perfectly vertical, the material failed prematurely and the test had to be repeated. To overcome these testing difficulties, flexural strength measurements were made using the 3-point bend method.

To identify any trends of statistical significance all data was analysed by two way analysis of variance (2-way-ANOVA; Appendix 6). Such an analysis is based on the following assumption.

The average value for any mechanical property for each formulation was noted. The variation of the formulation about the overall mean may be separated into component parts; the first corresponds to the variation between levels of BisGMA/THFMA, the second to the variation between levels of benzoyl peroxide, the third to the variation between interactions of BisGMA/THFMA and benzoyl peroxide, and the fourth corresponds to random error variation [69,70].

ie $Y_{ij} = \mu + \alpha_i + \beta_j + \alpha\beta_{ij} + \varepsilon_{ij}$ (22)

Y = response at A level i, B level j

α_j = effect of A at level i

β_j = effect of B at level j

$\alpha\beta$ = interaction of A and B

ε = error in response

Using an F-test, these components are compared to assess whether the variation between the levels of the two variables and their interactions are significant in relation to the experimental error (Appendix 6). This technique is called a two way analysis of variance or 2-way ANOVA. If there was a

significant difference between levels of the variables, a Scheffé s-test[71] (Appendix 7), was used to identify where the significant difference occurred. In an attempt to establish the variable values which would result in the maximum value of a mechanical property using BisGMA/THFMA and benzoyl peroxide, a step regression analysis, (Appendix 8), was employed to create a mathematical model which would relate the mechanical property to concentrations of BisGMA/THFMA and benzoyl peroxide [72].

All analyses were performed at $p \leq 0.05$ level of significance.

4.2 EXPERIMENTAL AND RESULTS

4.2.1 SAMPLE FORMULATION AND PREPARATION

A full factorial design was constructed for BisGMA/THFMA concentrations at five levels and benzoyl peroxide concentrations at three levels. This afforded an experiment which would involve fifteen observations.

Each of the fifteen process formulations differed only in the concentrations of BisGMA/THFMA and benzoyl peroxide. However, as a consequence of increasing the BisGMA/THFMA concentration, the time required for the dough to achieve the correct viscoelastic state necessary for moulding also increased. To illustrate this, the viscoelastic properties of a dough prepared with 40% BisGMA/THFMA and 3% benzoyl peroxide was measured in the oscillitory mode across frequencies of 0.01 H_Z to 10 H_Z as outlined in 2.2. At specific times after mixing, the viscoelastic properties of this dough were compared with the standard production dough.

Benzoyl peroxide (wt % of dough)	BisGMA/THFMA (% vol of liquid)				
	0%	20%	40%	50%	60%
0.72%					
2.16%					
3.6%					

Factorial Design for Effect of BisGMA/THFMA and Benzoyl Peroxide on Mechanical Properties

Process Variable	level
process pressure	4.5 tons
process temperature	175 C
EGDMA	20% of liquid
monomer/polymer ratio	1/2.3

Fixed Process Variable Levels

Each formulation was moulded using the mould described previously in Section 3.2.2. The surfaces of the test pieces were smoothed using emery paper (400 grade to 1200 grade). Any sample which had a surface flaw or inclusion was rejected.

Results

All of the fifteen formulations were processed with the exception of four: 40% BisGMA/THFMA and 3.6% benzoyl peroxide; 50% BisGMA/THFMA and 3.6% benzoyl/peroxide; 60% BisGMA/THFMA and 2.16% benzoyl peroxide; and 60% BisGMA/THFMA and 3.6% benzoyl peroxide. In these formulations, the benzoyl peroxide did not completely dissolve and, so, the final mouldings possessed inclusion of white benzoyl peroxide particles. Such inclusions would behave as stress concentrators and thus, weaken the matrix. As these samples were not tested this resulted in an incomplete or imbalanced design.

4.2.2 FLEXURAL STRENGTH

The flexural strength for each formulation was determined using a rectangular beam (50 mm x 7.9 mm and 20 mm) and an Instron TTCM.

The beam was rested on two supports which were 25 mm apart. Directly between the two supports, and on the opposite

side of the beam, was another support (Figure 16).

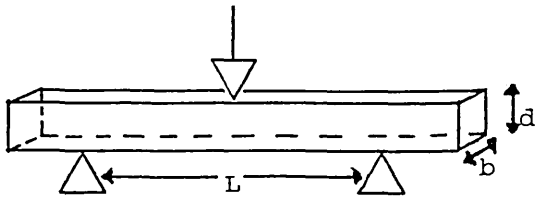


Figure 16 Three Point Bend Test for the Evaluation of Flexural Strength

The load was applied to the centre point of the sample at a strain rate of $1 \times 10^{-4}\ ms^{-1}$. The load required to fracture the specimen was noted. This procedure was repeated five times per formulation.

$$\text{Flexural strength} = \frac{3PL}{2bd^2} \qquad (23)$$

P = load at fracture

L = length of beam

b = breadth of beam

d = depth of beam

The average flexural strength for each formulation was noted and any significant difference between values for each formulation was tested using the 2-way Anova and Scheffé's test.

Results

Benzoyl peroxide concentration (% wt of dough)	BisGMA/THFMA concentration (% Vol of liquid)				
	0%	20%	40%	50%	60%
0.72%	157*	154(10.6)	146(6)	133(12.25)	69(5)
2.16%	155(7.3)	144(15)	156(7)	123(10.14)	NO DATA
3.6%	147(8.1)	148(14.8)	NO DATA	NO DATA	NO DATA

*Material did not fracture, but yielded, at this rate of strain. However, it was classified as a failure as the material had distorted out of shape by plastic yielding.

(Values in MPa. Figures in brackets are standard deviations).

Statistical Analysis

(a) Two way analysis of variance showed that there was a significant interactive effect between BisGMA/THFMA and the initiator.

(b) Scheffé's s-test showed that the only significant differences in flexural strength were between 40% and 50% BisGMA/THFMA and 40% and 60% BisGMA/THFMA.

(c) No mathematical model, with a good fit, could be found to relate the flexural strength to the BisGMA/THFMA concentration and benzoyl peroxide concentration.

4.2.3 YOUNG'S MODULUS

Method

The Young's modulus was determined in accordance to the method described in Section 3.2.4.

Results

Benzoyl peroxide (wt of dough)	BisGMA/THFMA concentration (%volume of liquid)				
	0%	20%	40%	50%	60%
0.72%	2.146 (0.12)	2.320 (0.33)	2.976 (0.17)	2.610 (0.13)	2.466 (0.10)
2.16%	2.130 (0.11)	2.48 (0.13)	3.222 (0.11)	2.930 (0.16)	NO DATA
3.60%	2.126 (0.09)	2.78 (0.03)	NO DATA	NO DATA	NO DATA

Modulus figures are in GPa.

Statistical Analysis

(a) There was an interaction between BisGMA/THFMA concentration and benzoyl peroxide.

(b) Scheffé's s-test showed the only significant difference in modulus was between 0% BisGMA/THFMA concentration and 40% BisGMA/THFMA concentration.

(c) The following mathematical model that related Young's modulus to BisGMA/THFMA concentration (Y) and benzoyl peroxide concentration (X) was derived.

$$E = 2.09 + 0.026Y - 0.00035Y^2 + 0.0049XY \qquad (24)$$

This model accounts for 71.2% of the total variation in modulus ($r^2 = 0.712$).

The model predicts the following BisGMA/THFM concentration which will afford the maximum modulus at fixed initiator concentrations:

Benzoyl peroxide (%wt of dough)	BisGMA/THFMA (% Volume of liquid)
0.72%	42.5%
2.16%	52.3%
3.60%	62.3%

4.2.4 SURFACE HARDNESS

Method

The method used to determine surface hardness was identical to the one described in Section 3.2.5.

Results

Benzoyl peroxide (%wt of dough)	BisGMA/THFMA concentration (%vol of liquid)				
	0%	20%	40%	50%	60%
0.72%	86.4 (.548)	87 (.707)	86.6 (.548)	87 (.707)	85.4 (.548)
2.16%	87 (.753)	87 (.548)	87 (.707)	87 (.707)	NO DATA
3.60%	86 (.707)	87 (.707)	NO DATA	NO DATA	NO DATA

Statistical Analysis

Changing neither the BisGMA/THFMA concentration nor the benzoyl peroxide concentration, significantly affected surface hardness.

4.2.5 VISCOELASTIC PROPERTIES

Method

The temperatures of the alpha relaxation, the elastic modulus at 158°C, and the damping factor at 37°C, were measured at 1Hz as specified in Section 3.2.6.

Results

(a) α-Relaxation Temperature (Tg)

Benzoyl peroxide (%wt of dough)	BisGMA/THFMA concentration (%volume of liquid)				
	0%	20%	40%	50%	60%
0.72	122	126	131	131	127
2.16	123	126	128	131	NO DATA
3.60	122	123	NO DATA	NO DATA	NO DATA

Statistical Analysis

Two way analysis of variance, (Appendix 6), showed that the Tg was significantly affected by BisGMA/THFMA concentration ($p \leq 0.05$). Regression analysis, (Appendix 8), gave the following model:

$$Y = 122 + 0.324X - 0.003542X^2 \quad (25)$$

Y = Tg (0°C)

X = BisGMA/THFMA concentration

($r^2 = 80.2\%$)

(b) Elastic Modulus at 158°C (MPa)

Benzoyl peroxide (wt% of dough)	BisGMA/THFMA concentration (%vol of liquid)				
	0%	20%	40%	50%	60%
0.72%	3.8	5.3	5.100	5.1	6.1
2.16%	8.330	8.20	5.105	5.5	NO DATA
3.60%	8.337	8.01	NO DATA	NO DATA	NO DATA

The samples for 40%/0.72%, 40%/2.16%, 50%/0.72%, and 50%/2.16% BisGMA/THFMA/benzoyl peroxide were all buckled after being tested. This distortion altered the geometry of the specimens and, possibly, reduced the accuracy of the results.

Statistical Analysis

Two way analysis of variance showed there was no significant effect on the elastic modulus at 158°C if either the benzoyl peroxide or BisGMA/THFMA concentrations were altered.

(c) Elastic Modulus at 37°C (GPa)

Benzoyl peroxide (%wt of dough)	BisGMA/THFMA concentration (%vol of liquid)				
	0%	20%	40%	50%	60%
0.72%	2.213	2.393	2.4	2.2	2.2
2.16%	2.52	2.366	2.489	2.1	NO DATA
3.60%	2.483	2.624	NO DATA	NO DATA	NO DATA

Statistical Analysis

The elastic modulus at 37°C was not significantly affected by altering the benzoyl peroxide concentration or the BisGMA/THFMA concentration.

(d) Tan δ at 37°C

Benzoyl peroxide (%wt of dough)	BisGMA/THFMA concentration (%vol of liquid)				
	0%	20%	40%	50%	60%
0.72%	0.072	0.069	0.063	0.064	0.065
2.16%	0.065	0.065	0.061	0.065	NO DATA
3.60%	0.066	0.061	NO DATA	NO DATA	NO DATA

Statistical Analysis

Two way analysis of variance, (Appendix 6), showed that only the benzoyl peroxide significantly affected tan δ at 37°C. However, regression analysis, (Appendix 8), provides a quadratic equation which modelled for tan δ using both benzoyl peroxide and the BisGMA/THFMA concentration.

$$Z = 7.22\times10^{-2} - 2.02\times10^{-3}X - 7.7\times10^{-5}Y + 1.0\times10^{-6}X^2Y^2 - 1.04\times10^{-4}XY \quad (26)$$

(r^2 = 73.27%) Z = tan δ at 37°C

X = Benzoyl peroxide concentration

Y = BisGMA/THFMA concentration

4.3 DISCUSSION

4.3.1 FLEXURAL STRENGTH

The analysis of variance showed that there was a significant interaction effect between the BisGMA/THFMA concentration and benzoyl peroxide concentration.

Scheffé's s-test determined that there was a significant decrease in flexural strength if the BisGMA/THFMA concentration was reduced from 40% to 50%. Increasing the concentration to 60% BisGMA/THFMA gave a further significant decrease in flexural strength. Below 40% BisGMA/THFMA there was no significant effect on the flexural strength. Increasing the BisGMA/THFMA concentration and benzoyl peroxide concentration from 0% and/or 0.72% respectively, changed the mechanism of failure from yielding to brittle fracture at the strain rate of 10^{-4} ms^{-1}.

This change in failure mechanism may be attributed to a reduction in molecular weight by increasing the benzoyl peroxide concentration and an increase in the degree of crosslinking with higher BisGMA concentration.

Both molecular weight and degree of crosslinking affect the strength of glassy polymers[21]. It is proposed that by increasing the BisGMA/THFMA concentration from 40% to 50%, this may show an increase in the degree of crosslinking above a critical value which results in a significant reduction in strength. Similar observations were made by Wollff[58] and Causton[63]. Both observed that increasing the crosslinking agent concentration, initially increases strength, but above a specific concentration strength falls rapidly. Addition

of BisGMA to the system may introduce two competing factors both of which affect strength. BisGMA has two aromatic rings in its structure, rendering it a rigid molecule. Inclusion of such chain stiffening functionalities into the backbone of a polymer chain increases strength[73]. However, BisGMA is also a dimethacrylate and will crosslink linear polymer chains. Increasing crosslinking will decrease strength. Therefore, as more BisGMA is added, the chain stiffeners tend to increase strength, whereas increased crosslinking may have the opposite effect. Increasing the concentration of BisGMA to 40% has no effect on strength and so both effects must cancel each other out. However, at the 50% level strength is reduced and so it may be assumed that the degree of crosslinking has increased above a critical value which the chain stiffening effect cannot attain.

Increasing the concentration of BisGMA/THFMA to 60% resulted in a further reduction in flexural strength. It was also observed that there was a fall in the modulus. These observations indicate that there is an increase in the amount of residual and/or pendant methacrylate groups in the network. Such groups will plasticise the polymer and reduce its strength[58,63]. These species will be present in greater concentration for two reasons. Firstly, as the number of BisGMA molecules present increases, the number of double bonds to be converted will correspondingly increase. As the time for conversion is fixed, the degree of conversion of the methacrylic double bonds will be decreased, thus affording more lower molecular weight chains having pendant methacrylate groups. Another possible reason

is also related to the degree of conversion the methacrylic double bonds. It has been reported[61] that the viscosity of a BisGMA type resin may affect the degree of conversion in BisGMA type resins. As the concentration of BisGMA/THFMA is increased, the viscosity of the comonomer increases and segmental mobility reduces. This may lead to a reduction in the degree of conversion of the methacrylate carbon double bonds[107], giving a greater concentration of pendant methacrylate groups and low molecular weight chains. Another consequence of the increased comonomer viscosity is that there might be incomplete wetting and poor mixing. This would give a matrix with reduced strength.

4.3.2 YOUNG'S MODULUS

As with the flexural strength, analysis of variance showed that there was a significant interaction effect between the BisGMA/THFMA concentration and benzoyl peroxide concentration. Scheffé's s-test determined that modulus was significantly increased by increasing the BisGMA/THFMA concentration from 0% to 40% and 50%. A mathematical model was found which expressed the modulus as a function of BisGMA/THFMA and benzoyl peroxide concentrations. The degree of fit is 71.2%.

$$E = 2.09 + 0.026Y - 0.00035Y^2 + 0.0049XY \qquad (24)$$

X = benzoyl peroxide concentration.

Y = BisGMA/THFMA concentration.

The equation shows that the most significant factors which effect modulus are the BisGMA/THFMA concentration (Y) and the interaction effect between benzoyl peroxide and BisGMA/THFMA (XY).

The model predicts the following: (95% confidence limits) if

if X = 0.72% then the maximum modulus is achieved at

42.5% BisGMA/THFMA
E = 2.68 ± 0.4390 GPa

X = 2.16% then the maximum modulus is achieved at

52.3% BisGMA/THFMA
E = 3.0 ± .4553 GPa

X = 3.60% then the maximum modulus is achieved at

62.3% BisGMA/THFMA
E = 3.402 ± .4191 GPa

However, at a BisGMA/THFMA level of 60%, it is not possible to add 3.6% level of benzoyl peroxide. The model does show that to maximise modulus, the BisGMA/THFMA concentration must be increased, but that the level of benzoyl peroxide must also be increased to fully polymerise the resin system and afford a greater modulus. The amount of benzoyl peroxide required increases with higher BisGMA/THFMA concentrations because there is a larger effective number of methacrylate double bonds that must be converted. If there is an insufficient concentration of benzoyl peroxide present, there will be less methacrylate groups converted, therefore, the quantity of lower molecular weight chains and pendant methacrylate groups will increase. This results in greater plasticisation and a lower Young's modulus.

The modulus is significantly increased at 40% and 50% BisGMA/THFMA concentration when compared to 0% BisGMA/THFMA for three possible reasons. At 40% and 50% BisGMA/THFMA levels, there may be sufficient chain stiffening aromatic groups present in the backbone of the polymer to effect an increase in the rigidity of the chain and, thus, increase the modulus. Also,

by increasing the BisGMA concentration, the propensity for crosslinking in the system is increased. The increased crosslinking will produce a higher modulus. Finally, at 40% and 50% BisGMA/THFMA, there may be sufficient THFMA present to effect a degree of antiplasticisation which will contribute to the improved modulus [12].

4.3.3 VISCOELASTIC PROPERTIES

Neither of the two modulus measurements, E'_{158} and E'_{37}, had statistically significant relationships with either benzoyl peroxide or BisGMA/ THFMA concentrations. This was surprising as the two variables did significantly affect the Young's modulus in tension.

The absence of a relationship is attributed to error in measuring E'_{37} and E'_{158} because some of the test sample bars buckled and distorted. This changed the dimension of the bars giving an inaccurate value for E'. The buckling, during heating above Tg in the analysis, may be being induced by anisotropy which is a result of transfer moulding these formulations.

However, as this error would be present in the storage and loss modulus, the tan δ values would be error free, as any error would cancel out (assuming it to be constant).

$$\tan \delta = \frac{E'' \times \text{error}}{E' \times \text{error}}$$

Both tan δ at 37° and Tg measured at 1 Hz were significantly affected by benzoyl peroxide concentration and/or the BisGMA/ THFMA concentration.

(a) α- Relaxation Temperature, Tg

Two-way analysis of variance, (Appendix 6), showed that Tg was significantly affected by the BisGMA/THFMA concentration ($p \leq 0.05$). Regression analysis, (Appendix 8), afforded a model which showed that the relationship between BisGMA/THFMA concentration and Tg was parabolic.

$$Tg = 122 + 0.324X - 0.06354X^2 \quad (25) \quad (r^2 = 80.2\%)$$

X = BisGMA/THFMA concentration

Tg is at a maximum when BisGMA/THFMA concentration is 45.76% (95% confidence limits).

The increase in Tg with increasing BisGMA/THFMA concentration up to 45.76% may be due to the fact that up to this concentration, the BisGMA/THFMA is being incorporated into the matrix with a high degree of conversion of the methacrylic double bonds. This would produce a system which has a stiffer backbone due to the inclusion of the aromatic group in the BisGMA. The effect of such chain stiffening groups is to increase the Tg [10]. The Tg may also be increased by an increased crosslink density [37]. The crosslink density would be greater because the number of dimethacrylates has increased. A higher degree of conversion of the methacrylic double bonds may give a reduced quantity of pendant methacrylate groups and lower mechanical weight chains. This would in turn yield a smaller degree of plasticisation [54], and depression of Tg [37]. The degree of antiplasticisation may also be decreased by an increased concentration of THFMA in the backbone [12], again, affording an increase in Tg.

(b) Tan δ at 37 C

A two-way ANOVA, (Appendix 6), of the data showed that only the benzoyl peroxide concentration significantly affected tan δ at 37°C. However, the degree of fit of a regression analysis of tan δ and the benzoyl peroxide and BisGMA/THFMA concentrations was improved if both variables were included - inferring an interaction effect.

$$\tan \delta_{37°C} = 7.22\times10^{-2} - 2.02\times10^{-3}X - 7.7\times10^{-5}Y + 1.0\times10^{-6}X^2Y^2 - 1.04\times10^{-4}XY \quad (26)$$

(r^2 = 73.27%) X = benzoyl peroxide concentration

Y = BisGMA/THFMA concentration

The model shows that the relationship between tan δ and the benzoyl peroxide concentration and BisGMA concentration is a quadratic in X and Y. Therefore, if a three dimensional plot of the relationship between these three factors was made it would be parabaloid (Figure 17).

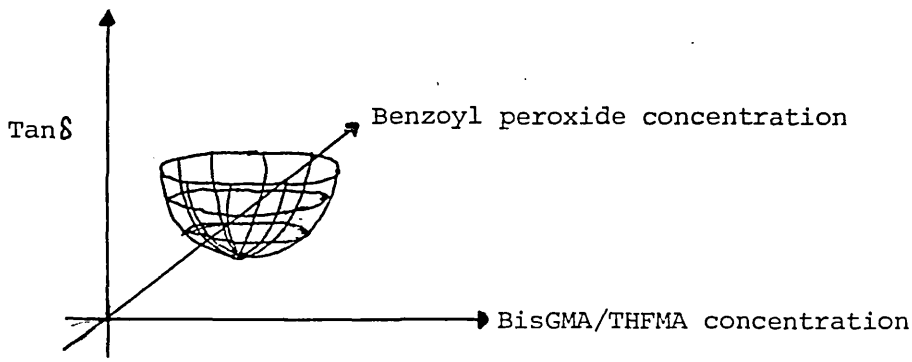


Figure 17 Parabaloid Relationship Between BisGMA/THFMA, Benzoyl peroxide, and Tan δ

Solving the model by first differentiating the equation then using the Newton-Raphson method[74] leads to the prediction that tan δ will be a minimum when the BisGMA/THFMA concentration is 36.36% and the benzoyl peroxide concentration is 1.375%. The model predicts that

at a given value of BisGMA/THFMA, the tan δ at 37°C will decrease to a minimum value as the benzoyl peroxide concentration increases. However, as the benzoyl peroxide concentration increases above a critical value the tan δ at 37°C will also increase. The model may be explained in terms of network structure in the following manner. As the benzoyl peroxide concentration is increased, the degree of conversion of the methacrylic double bonds will be increased. This will afford a system which has less pendant methacrylate groups and lower molecular weight chains. Thus, the system will be less plasticised and so tan δ will be smaller. Also, if the degree of conversion is increased, the crosslink density may also be raised to yield a lower tan δ[43]. However, if the benzoyl peroxide concentration is increased beyond a critical level, it may give a reduced molecular weight as molecular chain length, and therefore molecular weight, is dependent on the square root of the initiator concentration. The reduction in molecular weight might result in an increase in tan δ.

The model also predicts that at a given concentration of benzoyl peroxide tan δ at 37°C will decrease to a minimum value as the concentration of BisGMA/THFMA is increased. If the BisGMA/THFMA concentration is increased beyond a critical level the tan δ at 37°C will once again increase. The model may be rationalised in terms of network structure by considering that as the BisGMA/THFMA concentration is increased, the number of methacrylic double bonds also increases. However, there must be a

finite number of double bonds with which a fixed benzoyl peroxide concentration can react within the given time cycle. If this critical number of double bonds is exceeded, then there will be a lower degree of conversion and a greater number of lower molecular weight chains and pendant methacrylate groups. Such groups would plasticise the network giving an increased tan δ[110]. A reduced degree of conversion may yield a lower crosslinked density which might also increase tan δ[43] as the propensity for molecular movement will be less restricted. At the optimum BisGMA/THFMA and benzoyl peroxide levels, the minimum tanδ, and therefore the rate of creep[43], will be achieved because there will be less pendant methacrylate groups present to plasticise the network. Also, there will be an increased amount of BisGMA which will result in a greater rigidity and therefore reduced flexibility in the polymer chains[39]. Also, a higher concentration of THFMA may afford increased antiplasticisation[12]. Both of these effects will reduce the propensity for polymer molecule viscous flow, and, thus result in a lower tanδ.

4.3.4 SURFACE HARDNESS

There was no significant differences in the surface hardness of the materials processed, (Appendix 6). As was discussed in Chapter 3, (Section 3.3.3), this might arise because, although the degree of conversion for each each system may be similar, the network structure might be completely different. This is a possible reason why the hardness of the materials are similar but other mechanical properties, for example, tensile strength and

modulus, which are dependent on network structure, are different.

However, as was also discussed in Chapter 3, the Shore durometer may not have the required sensitivity to detect the differences in structure of the systems studied.

4.4 CONCLUSIONS

The flexural strength of a tooth material is not significantly reduced ($p \leq 0.05$) by the addition of BisGMA/THFMA up to a concentration of 50% BisGMA/THFMA. At concentrations of BisGMA/THFMA, greater or equal to 50% flexural strength is significantly decreased.

Addition of BisGMA/THFMA to a system which has a benzoyl peroxide concentration of 0.72%, changes the mechanism of failure from yielding to fracture.

There is an interaction between the benzoyl peroxide and BisGMA/THFMA concentration which significantly affects the Young's modulus ($p \leq 0.05$). The effect is described mathematically by the following equation:

$$E = 2.09 + 0.026Y - 0.00035Y^2 + 0.0049XY \qquad (24)$$

($r^2 = 71.2\%$) E = Young's modulus

X = benzoyl peroxide concentration

Y = BisGMA/THFMA concentration

The model states that the Young's modulus is affected most by the BisGMA/THFMA concentration and the interaction between benzoyl peroxide and BisGMA/THFMA concentrations.

The greater the concentration of BisGMA/THFMA present, more benzoyl peroxide is required to achieve the maximum modulus.

The viscoelastic parameters: the alpha relaxation temperature (Tg), and the damping coefficient ($\tan\delta$) are significantly affected by the BisGMA/THFMA and benzoyl peroxide concentrations ($p \leq 0.05$). The following mathematical model

describes how the Tg is affected by the BisGMA/THFMA concentration:

$$Tg = 122 + 0.324X - 0.00354X^2 \qquad (25)$$

$(r^2 = 80.2\%)$

where X = BisGMA/THFMA concentration.

The relationship between Tg and the BisGMA/THFMA concentration is parabolic with the maximum Tg occurring at 46% (95% confidence limits) BisGMA/THFMA concentration.

The value of $\tan \delta_{37}$ is predicted by the following model:

$$\text{Tan}\,\delta_{37} = 7.22\text{x}10^{-2} - 2.02\text{x}10^{-3}\,X - 7.7\text{x}10^{-5}\,Y + 1\text{x}10^{-6}\,X^2Y^2 - 1.04\text{x}10^{-4}\,XY \qquad (26)$$

where X = benzoyl peroxide concentration $(r^2 = 73.27\%)$

Y = BisGMA/THFMA concentration

Surface hardness is not significantly affected ($p \leq 0.05$) by the concentrations of benzoyl peroxide or BisGMA/THFMA, although the Shore durometer may not be sensitive enough to detect differences between formulations.

The optimum resin formulation is 40% BisGMA/THFMA and 2.16% benzoyl peroxide. This formulation gives optimum stiffness, viscoelastic behaviour, and surface hardness without sacrificing strength.

Chapter 5: STUDY OF THE EFFECT OF SUBSTITUTING PMMA WITH AN ORGANOSILANE COATED SILICA

5.1 INTRODUCTION

Previous researchers have investigated the effects of filler particles in the mechanical properties of composites.[75-85] The aim of this part of the Thesis is to examine the effect of fine particle size silica filler level on the processing and mechanical properties of an acrylic resin containing 40% (vol of liquid) BisGMA/TMFMA and 2.16% (by weight) benzoylperoxide.

5.1.1 ADVANTAGES OF POLYMER COMPOSITES IN DENTISTRY

The technology of polymer composites in dentistry has greatly improved since their introduction in the 1950's[87]. By reinforcing acrylic resins with inorganic fillers, it was hoped that a clinically superior filling material could be developed. However, early formulations were inferior to today's composites[88] because they contained resins with high polymerisation shrinkage, and also, the principles of reinforcement, in particular the requirement for coupling between filler and resin, and the effect of different filler types and particle sizes on the mechanical properties of the composite were not fully understood.

In 1962 R L Bowen[55] synthesised 2,2-bis [4,(2-hydroxy-3-methacryloxy propoxyphenyl)] propane, BisGMA, which overcame some of the limitations of MMA resins, such as: insufficient stiffness, large polymerisation shrinkage and a high coefficient of thermal expansion.

Later it was found that the mechanical properties of filled resins were improved if a coupling agent such as γ-methacryloxypropyltrimethoxysilane was condensed onto the

silica filler particle surface prior to polymerisation[89]. During polymerisation the silane, which is chemically bonded to the silica, bonds to the resin thus giving, ultimately, an interfacial bond between the filler and the resin. The nature of the interfacial bond is complex and may be both physical and chemical[90]. The role of the coupling agent may be purely as a bridge which transfers applied stresses from one phase to another. It has also been proposed that silanation ensures that the filler surface is clean by reducing water sorption[91]. Another possible reason why organosilanes may improve the mechanical properties of the composite is because they apparently enhance dispersion of filler in the resin. This affords better wetting of the filler and, possibly, higher filler loadings[91]. Filler loading may also be increased by use of spherical particles and an intermittent size distribution[92]. Most commonly used filler particle sizes vary between 0.04 μm and 20 μm - micro and macroparticles respectively[93]. The different particle sizes have both advantages and disadvantages when viewed in isolation, and so a current trend is to use combinations to achieve the advantages from each[45]. Composites currently available have up to 76% volume fraction filler content and an elastic modulus of 16 GPa[87]. Conventional dental acrylics have a Young's modulus of 2.6 GPa[87]. Other mechanical properties in which composites are superior to acrylics have been reported to be:[87] compressive and tensile strength; thermal expansion; and dimensional changes on polymerisation. Water sorption is also lower for composites and reduces as filler content increases.[45,87]

Soderholm[94] has shown that water absorption reduces the mechanical properties of a dental composite by plasticising the resin, and possibly by hydrolysing of the interfacial bond between resin and filler.

Despite the growth in the number of different brands of polymer composite restorative materials there are only a few types of composite acrylic teeth available, for example, "Orthosit" by Ivoclar and "Crystal ND" by Major dent. These filled teeth were first introduced in the 1970's.[4] Their design is such that the labial portion of the tooth is a composite and corresponding lingual layers are unfilled (Figure 18).

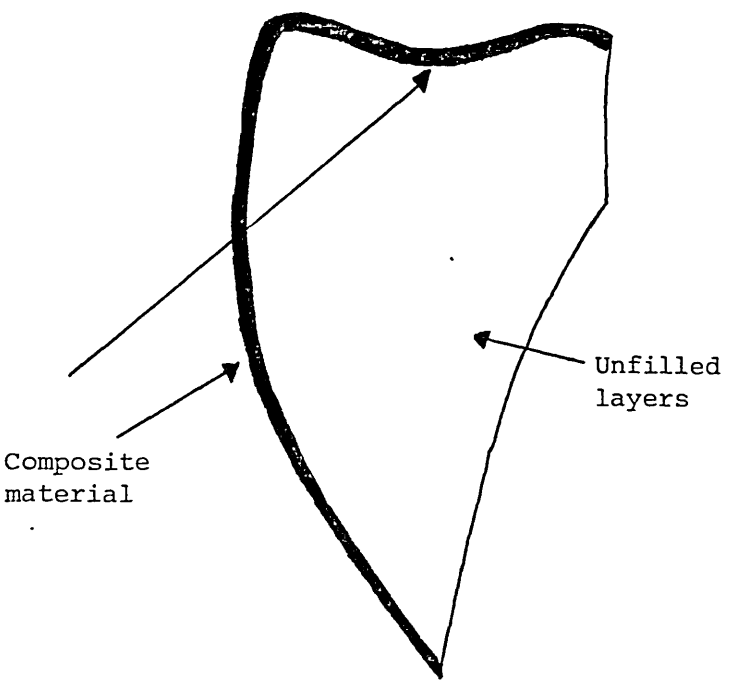


Figure 18 Cross Section of "Abrasion Resistant" Acrylic Teeth

Such a design means that the technician may easily trim the lingual layer when articulating the denture, yet the filled labial tooth surface is harder, has greater rigidity, and greater abrasion resistance[10] than the conventional dental acrylic.

5.1.2 THE EFFECT OF REPLACING PMMA WITH INORGANIC FILLER ON THE RHEOLOGY AND PROCESSING OF THE MONOMER/POLYMER DOUGH

Addition of a filler to a resin will increase viscosity, modify flow patterns, render the system thixotropic or shear thinning, and increase mould wear during processing[91]. As the quality of polymer is being reduced and replaced with an inorganic phase which will not interact with the monomer in the same fashion, this will perhaps result in the system having a greater viscous component and less elastic than the conventional monomer/polymer dough.

Important properties of the filler in determining the rheologic and processing characteristics of the dough include[91]: concentration, particle size and distribution, shape, stiffness, strength and the specific ability of the resin to wet the filler.

Two critical steps in the processing of the composite are mixing and dispersion of the filler in the resin. If the filler is not evenly distributed throughout the resin this may lead to composition gradients and agglomeration of particles. Both of these will afford poorer mechanical properties[91]. A composite is properly mixed when the filler and resin are statistically, evenly, distributed within the space the composite occupies[95] (Figure 19).

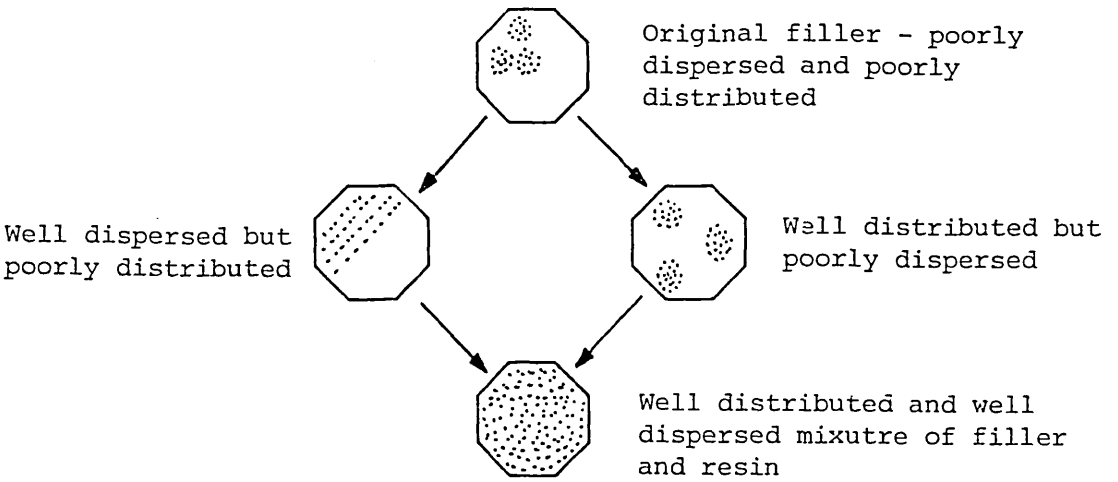


Figure 19 Mixing and Dispersion of Composites

Dispersion is involved in the breakdown of agglomerates. Dispersion involves: initial wetting, breakdown of agglomerates (of filler particles to discrete filler particles), followed by intimate wetting of particles[91]. Dispersion becomes more difficult as particle size decreases. Also, the agglomerates are most easily dispersed when the shear forces are above a specific critical value. Therefore, processing of a formulation may have as great an effect on the mechanical properties of the composite as the components of the formulation. If the processing is poorly executed, then the mechanical properties of the composite will be reduced.

5.2 EXPERIMENTAL AND RESULTS

5.2.1 MIXING, DISPERSION AND RHEOLOGY

(a) Preparation of the Resin

The components of the resin are listed below.

Component	Concentration
BisGMA/THFMA	40% by vol of resin
EGDMA	20% by vol of resin
MMA	40% by vol of resin
Benzoyl peroxide	2.16% by weight of mix

The resin constituted 27% (by volume) of the composite.

(b) Mixing and Dispersion of the Silica Filler in the Resin and Moulding of the Composite

(i) Mixing and dispersion

Method

Each composite mixture contained 27% of resin and 73% solids. The solids were PMMA and silica coated with γ-methacryloylpropoxytrimethoxysilane.

The silica had an average particle size of 2 μm, and so may be classed as a fine particle filler[45]. Composites were prepared which had 25%, 50%, 60% and 75% vol fraction of silica. The composites were processed as shown in Figure 20.

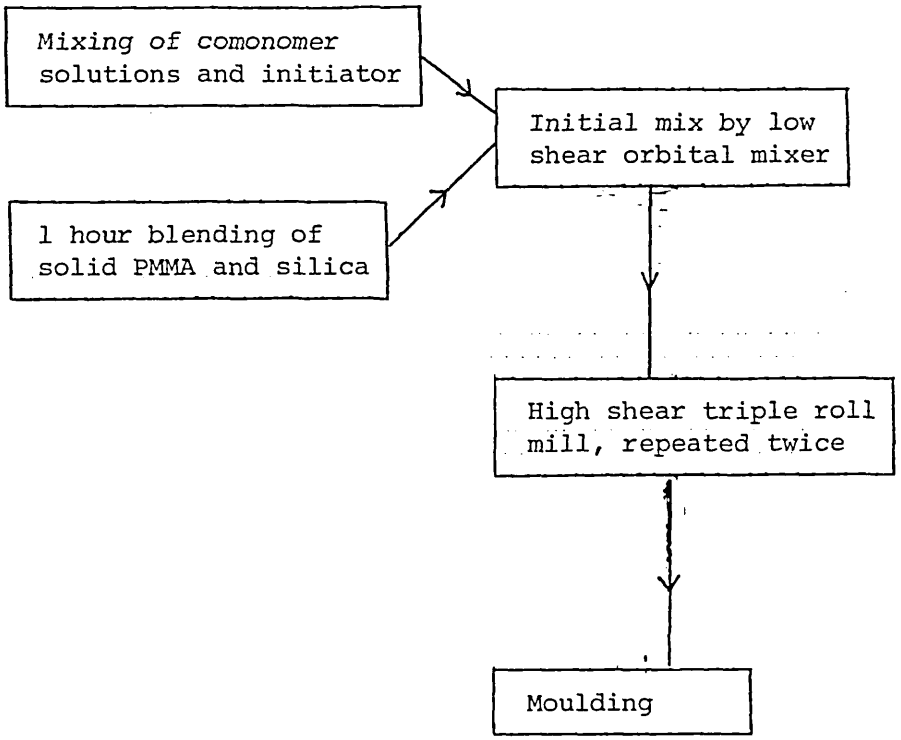


Figure 20 Flow Chart for Processing of Composites Resins

The composite resins were moulded before being passed through the triple mill, and then after being passed through once, then twice.

Results

Every composite had visible agglomerates of filler particles if they were moulded before they were passed through the triple mill for the second time - irrespective of the moulding technique employed. After the composites were passed through the triple mill for the second time the agglomerates were dispersed except in the case of the 75% silica. These particles did not fully wet during mixing and jammed the triple mill.

(ii) Moulding and rheology

Method

Each composite mix was moulded by: transfer, pseudo compression, and compression moulding. Moulding was carried out at 175 °C after being conditioned for three days at 23 °C. The dynamic viscosity and storage modulus of each mix was determined two hours after mixing.

Results

As more filler was added the doughing time increased - the material had a greater degree of viscous flow and was less elastic in nature.

Concentration of filler in the composite (v/v)	G'min (0.01 Hz)	G'max (10 Hz)	η'min (10 Hz)	η'max (0.0 Hz)
0%	22,810	202,000	597.4	328,500
25%	*	47,390	477.6	*
50%	7,389	46,900	411.6	181,600
60%	5,474	34,210	202.5	155,400

(*No data is reported for 25% Silica at 0.01 Hz because the instrument either could not apply the correct strain amplitude or the data was not within limits of ± 10%.)

The Dynamic Viscosity and Storage Modulus of Volume Fractions of Silica 2 Hours after Mixing.

The composites, as a consequence of the increased viscous component in their flow, could not be successfully transfer or pseudo compression moulded. Despite altering pressure from 1 to 6 tons, all mouldings were porous on the surface.

However, successful mouldings were afforded by compression moulding the composites. The conditions for moulding are given below. If the pressure was increased above 3 tons, the material leaked from the mould giving a porous moulding. If the pressure was reduced below 3 tons, the pressure was not great enough to remove all of the air from the moulding, yielding a porous structure.

Pressure	3 tons
Temperature	175 °C
Time cycle	4 minutes heating, 4 minutes cooling
Material condition	snap dough stage (approximately 3 days after mixing

Optimum Conditions for Compression Moulding of Components

5.2.2 FLEXURAL STRENGTH

Method

This was carried out in accordance to the method outlined in section 4.2.2.

Results

Concentration of filler in the composite (v/v)	Flexural Strength
0% Silica filler	155 MPa (SD = 7.00)
25% Silica filler	92 MPa (SD = 7.00)
50% Silica filler	119 MPa (SD = 11.20)
60% Silica filler	141 MPa (SD = 7.39)

Statistical analysis: The means of the flexural strength of each formulation were compared using Student's t-test ($p \leq 0.01$) (Appendix 4). The t-test showed:

(a) Addition of 25% (v/v) and 50% silica filler very significantly decreased flexural strength ($p \leq 0.01$). Addition of 60% silica filler significantly decreased flexural strength ($p \leq 0.05$).

(b) Increasing the silica concentration from 25% to 50% significantly increased flexural strength.

(c) The flexural strength of the composite which contained 60% silica was significantly greater than that of the composites with 50% and 25% silica.

5.2.3 MODULUS OF ELASTICITY IN BENDING

Method

The modulus of elasticity in bending was determined using the load deflection curve obtained in the analysis of flexural strength (Section 5.2.2). A tangent was drawn to the steepest initial portion of the load deflection curve. The modulus of elasticity in bending, E_B, is given by:

$$E_B = \frac{L^3 M}{4bd^3} \qquad (27)$$

where L = length of support (m)
M = gradient of tangent (N/m)
b = sample breadth (m)
d = sample depth (m)

Results

Filler concentration	Modulus in Bending (GPa)
0%	3.68 (SD = 0.10)
25%	5.294 (SD = 0.28)
50%	12.706 (SD = 2.5)
60%	13.07 (SD = 0.88)

Statistical analysis by the Mann-Whitney-U-test (Appendix 9), showed that increasing the filler level from 0% to 25% and then from 25% to 50% caused an increase in modulus. However, there was no statistical increase in modulus when the filler volume fraction was increased from 50% to 60%.

5.2.4 SURFACE HARDNESS

Method

The surface hardness was determined as outlined in Section 3.2.5.

Results

Concentration of filler in the composite (v/v)	Surface hardness
0%	87 (SD = 0.707)
25%	90 (SD = 0.447)
50%	93 (SD = 0.707)
60%	95 (SD = 0.707)

Statistical analysis:

Analysis of the means using Student's t-test showed that there was a significant increase in surface hardness at silica.filler levels of 25%, 50% and 60% silica.

5.2.5 VISCOELASTIC PROPERTIES

Method

The storage modulus at 37°C and 158°C measured at 1 Hz, the alpha relaxation temperature at 1 Hz, and the damping factor at 37°C, were determined using the method outlined in Section 3.2.6.

Results

The following results were extracted from the DMTA spectra in Figures 21 - 26.

Composite	$E'_{37°C}$ (GPA)	$\tan\delta_{37°C}$	T_α	$E'_{158°C}$ MPa
0% Silica	2.49 (SD=0.25)	0.061 (SD=0.0035)	127°C	5.1 (SD=0.25)
25% Silica (SI25)	2.84 (SD=0.197)	0.053 (SD=0.003)	120°C	1.406×10^2 (SD=.20)
50% Silica (SI50)	3.62 (SD=0.30)	0.044 (SD=0.0028)	117°C	7.72×10^2 (SD=2.8)
60% Silica (SI60)	3.82 (SD=0.25)	0.042 (SD=0.00)	115°C	1.18×10^2 (SD=.32)

The E'_{37}, $\tan\delta_{37}$ and E'_{158} values were compared using Student's t-test ($p \leq 0.05$) (Appendix 4).

(a) Storage modulus at 37°C increased significantly with the addition of 25%, 50% and 60% silica. Significant increases were also observed between the 25% and 50%, the 25% and 60%, but not the 50% and 60% levels.

(b) There was a significant decrease in tan δ with the addition of 25%, 50% and 60% silica. Significant decreases in tan δ were also observed between the 25% and 50%, the 25% and 60%, but not the 50% and 60% filler levels.

(c) Storage modulus at 158 °C increased significantly when 25%, 50% and 60% silica was incorporated into the resin. Significant increases were also observed between the 25% and 50%, the 25% and 60%, but not the 50% and 60% filler levels. In all cases, the storage modulus at 158 C was different where the level of significance was less than 1%.

(d) Although they were not analysed statistically, because there was no detectable deviation in three sets of data, the alpha relaxation temperature decreased with increasing silica content.

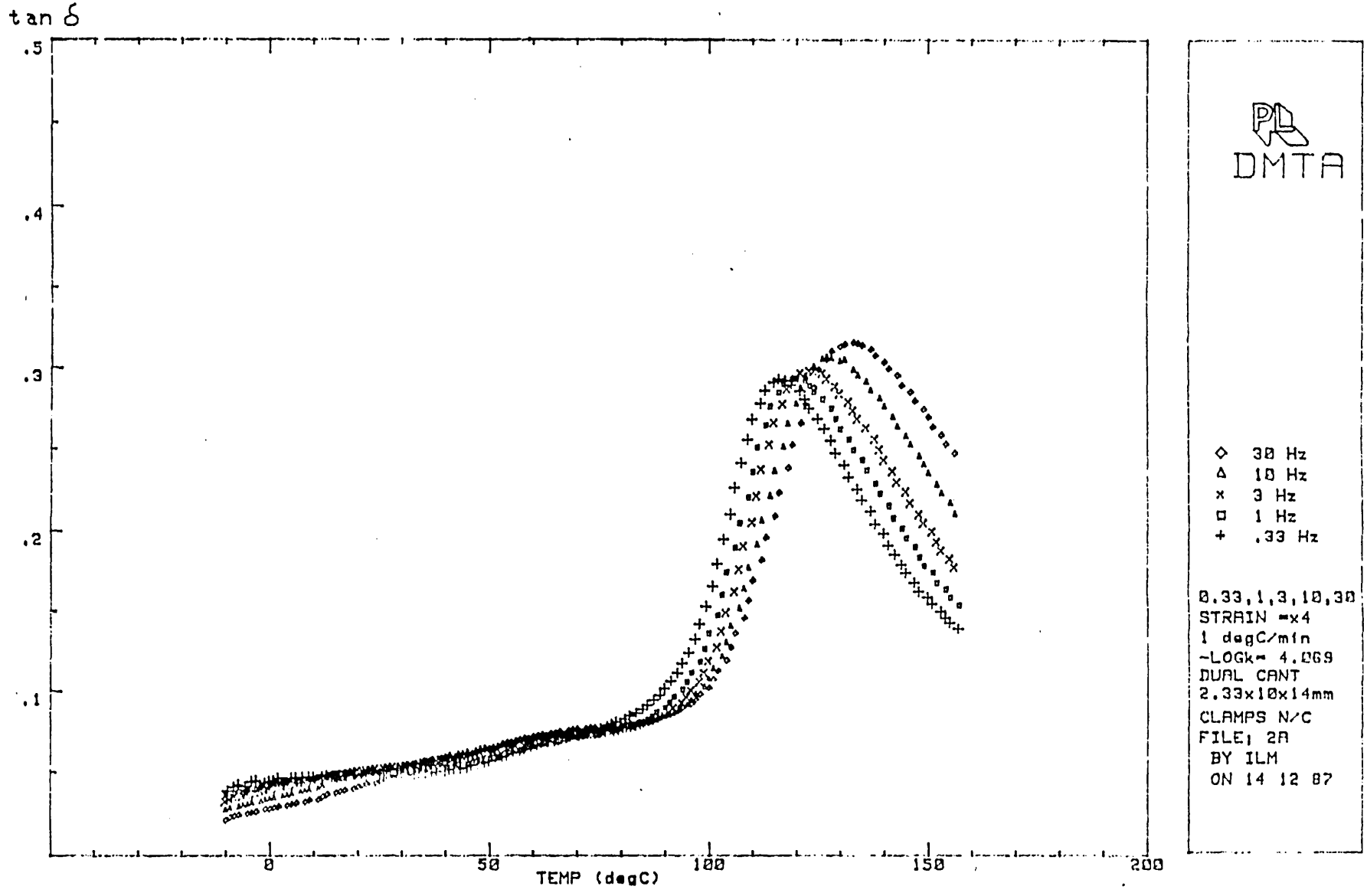


Figure 21 Tan δ V's Temperature for 25% Volume Fraction Silica

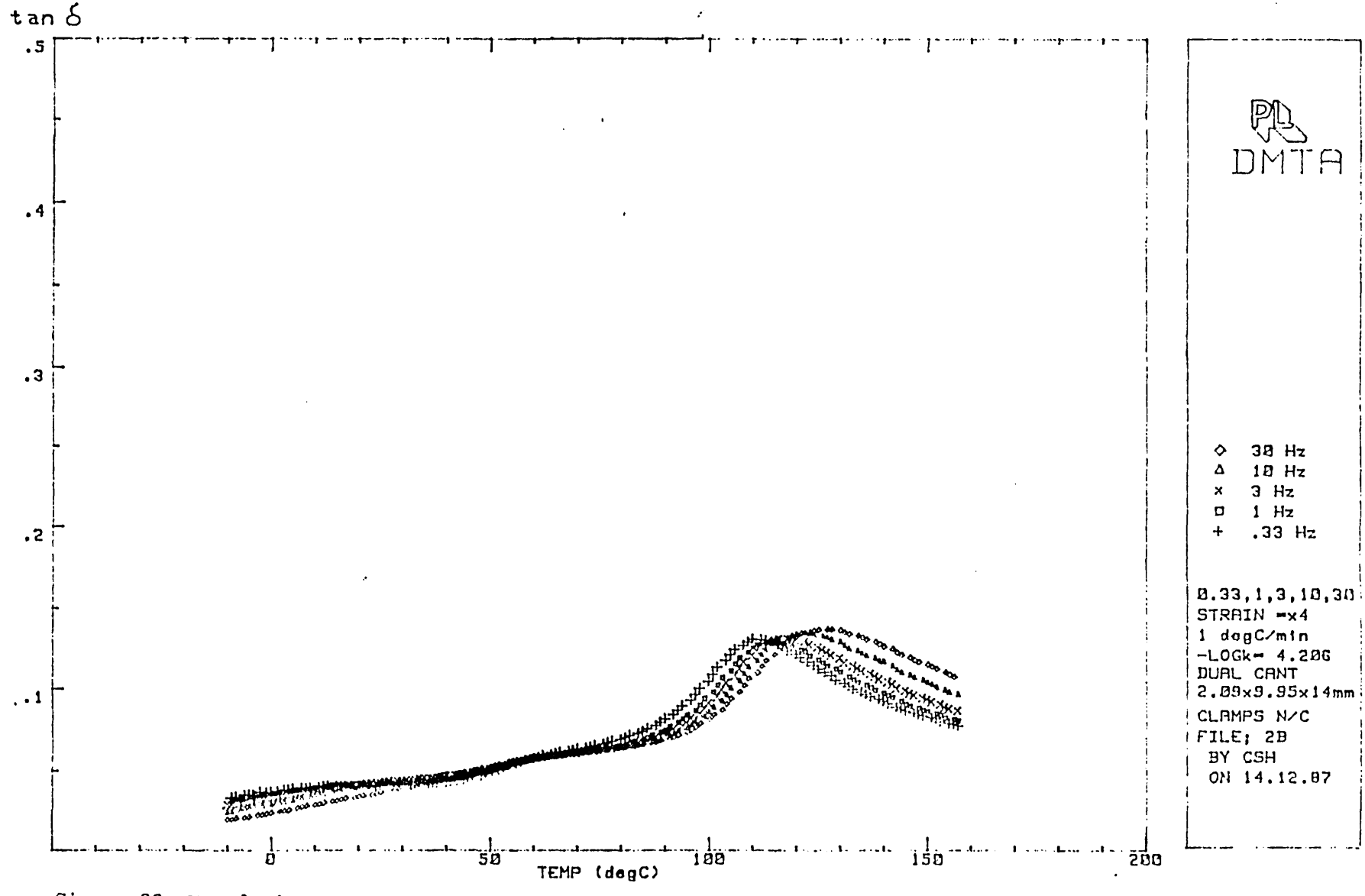


Figure 22 Tan δ V's Temperature for 50% Volume Fraction Silica

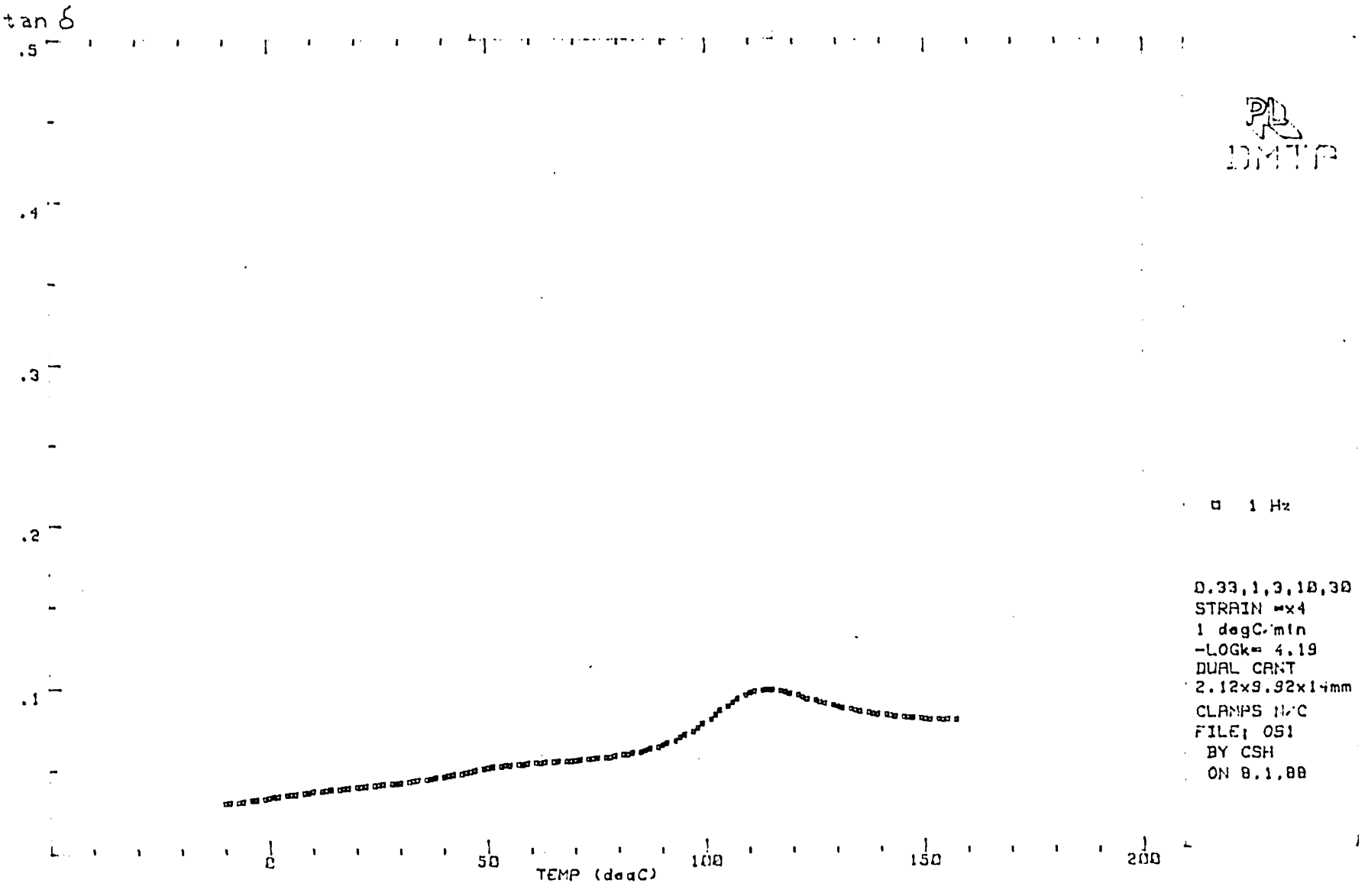


Figure 23 Tan δ V's Temperature for 60% Volume Fraction Silica

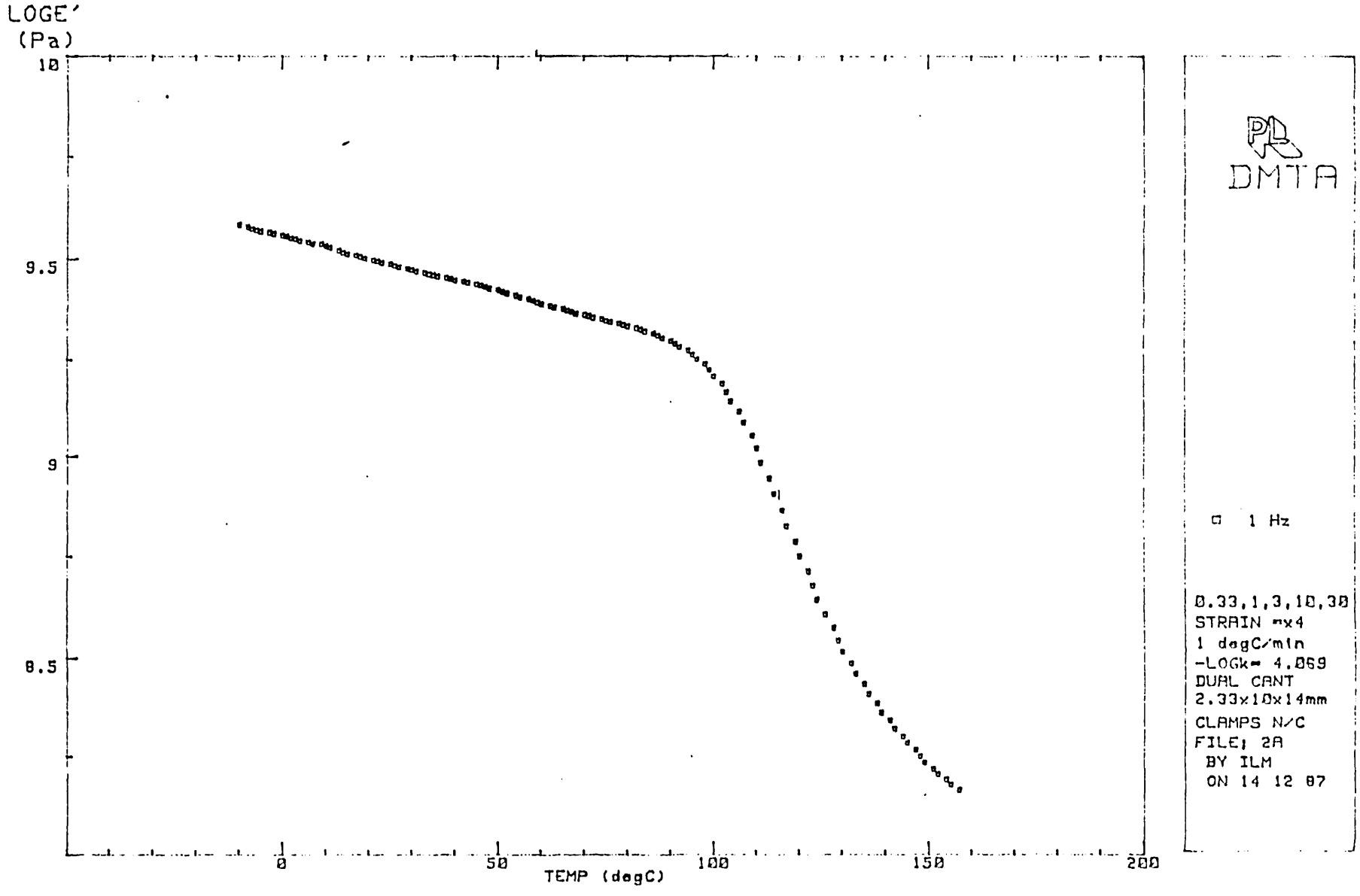


Figure 24 Log Storage Modulus V's Temperature for 25% Volume Fraction Silica

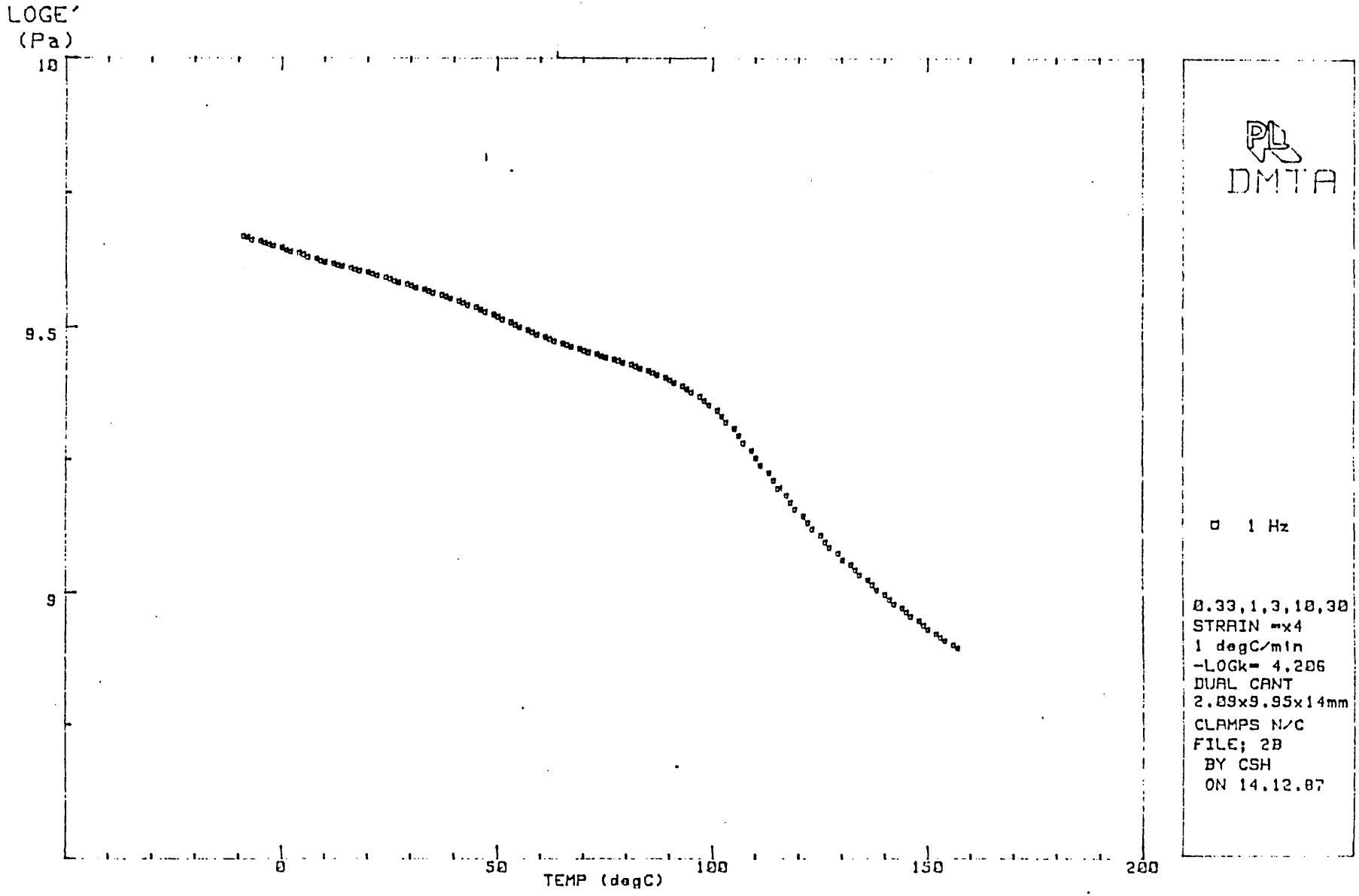


Figure 25 Log Storage Modulus V's Temperature for 50% Volume Fraction Silica

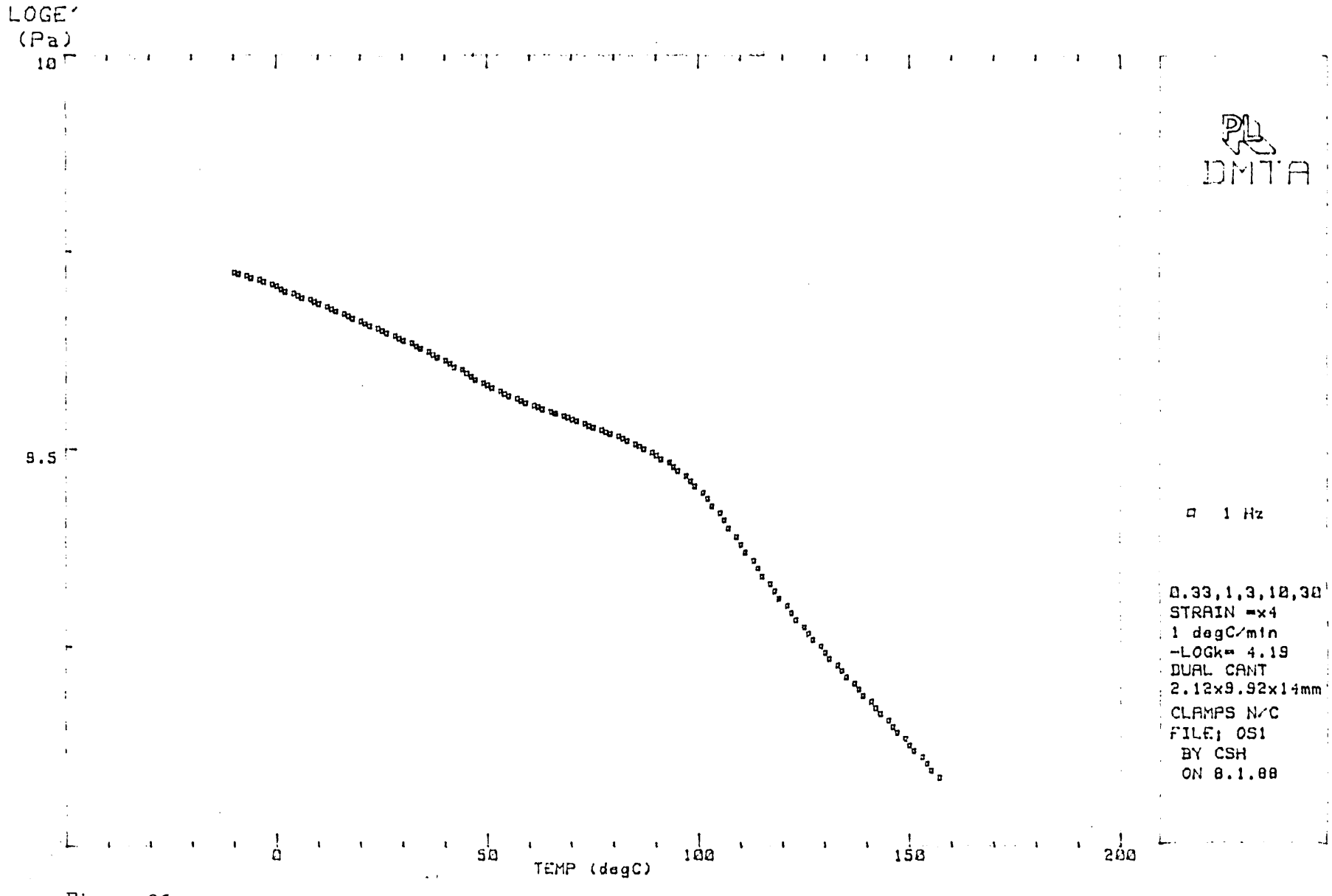


Figure 26 Log Storage Modulus V's Temperature for 60% Volume Fraction Silica

5.3 DISCUSSION

5.3.1 EFFECT OF FILLER CONTENT ON THE MIXING AND DISPERSION OF THE COMPOSITE

In order to achieve a composite, which on moulding had no visible agglomerates of filler, the mixes had to be subjected to a two step mixing process. The low shear orbital mixing was necessary to initially wet all of solid - whether the solid was in the form of discrete particles or agglomerates of particles. When the materials were moulded at this stage the resulting mouldings had visible agglomerates of filler. Thus, insufficient shear forces had been applied to break down the agglomerates[91]. When the materials were passed once through a triple roll mill then moulded, the mouldings still had agglomerates but to a lesser degree. Some of the agglomerates had been dispersed by the higher shear forces applied by the mill. A second pass through the mill was sufficient to disperse all of the agglomerates except for the case of 73% silica.

When 73% of the total volume of the mixture was silica the resin is unable to wet all of the solid as the surface area of the solid particles is too high for the volume of liquid to wet. At this level of filler loading the material was so dry that it stopped the triple mill. Also, the removal of the solid polymer reduced the breadth of the particle size distribution. This may afford less efficient packing of the solid and thus reduce the critical volume fraction that a given liquid system will wet.

5.3.2 EFFECT OF FILLER CONTENT ON THE RHEOLOGICAL PROPERTIES OF THE COMPOSITE

As the frequency of oscillation was increased, the dynamic viscosity of the formulations, at all filler levels, fell. Thus, the composites were shear thinning. This is in agreement with measurements on commercial composites carried out by others[96,97]. Generally, replacing the solid PMMA with silica, reduced the viscosity and rigidity of the mixture. Thus, the resistance to flow and degree of network in the mixture is reduced as the silica content is increased and the polymer content reduced. This observation may be attributed to the fact that as PMMA is removed there is less material for the monomer to interact or "dough" with, and so the quantity of polymer/monomer gel/dough network will be smaller.

The effect of increased flow properties with higher silica content on compression moulded composites, was that the test pieces produced had greater flash and a thinner section if all formulations were processed at the same time under identical conditions. For example, test pieces produced from the 25% silica composites had an average depth of 2 mm but the 60% silica composites had an average depth of 1 mm.

5.3.3 EFFECT OF SILICA CONTENT ON THE MOULDING PROCESS

(a) Transfer Moulding

With the exception of the resin which had no silica, all mouldings had porosity. The porosity was caused by entrapped gases on the surfaces of the moulding. The gas is not evacuated from the mould due to a lack of pressure. As the composite resins have greater flow properties they

leak from the cavities and out of the mould. Therefore, pressure cannot be maintained, and the gas is not effectively displaced from the cavity by resin.

The reduction of pressure may allow the boiling of the monomer during the curing cycle as the cavity pressure is reduced, and thus, the boiling point will be reduced. Hence the porosity may be air or gaseous monomer. The surface porosity may also be due to polymerisation shrinkage[45] which has not been compensated for by flow of excess material from the transfer pot.

(b) Pseudo Compression Moulding

Again all mouldings had porosity on the surface due to lack of pressure caused by excess flashing of material from the cavity. The porosity was more pronounced than in transfer moulding, suggesting that the pressure was lower in this case, affording a lower boiling point for the monomer and less material to compensate for any polymerisation shrinkage.

(c) Compression Moulding

A special compression mould was made by transfer moulding a piece of acrylic into a deepened cavity. This acrylic became the male part of a two-part compression mould - the female cavity being the cavity the acrylic was moulded from (Figure 27). This not only afforded a good edge fit, but due to the fact that the acrylic expanded as temperature was increased, it gave a better seal resulting in less material leakage.

The reduction in leakage gave increased pressure which forced the gases from the cavity, yielding porous-free mouldings. It was noted that the thickness of the mouldings decreased with increasing silica content. This observation is a result of the increased flow properties of the higher silica concentration resins.

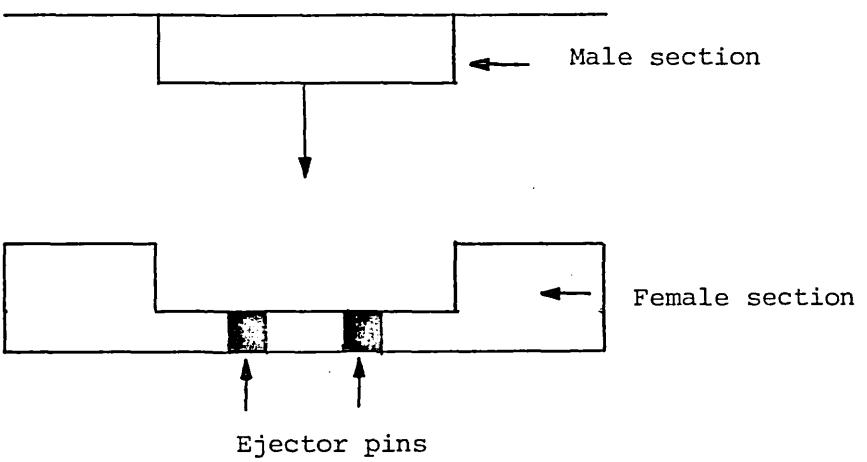


Figure 27 Two part Compression Mould

5.3.4 EFFECT OF SILICA CONCENTRATION ON FLEXURAL STRENGTH

Incorporation of silica particles in the resin significantly decreased the flexural strength. However, by increasing the silica concentration the flexural strength significantly increased - although it did not return to the strength of the unfilled resin.

Given that for fracture stress, σ,

$$\sigma = \left(\frac{EG_{ic}}{\pi C_0} \right)^{\frac{1}{2}} \qquad (28)$$

where E = Young's modulus
C_0 = Inherent flaw size
G_{ic} = Critical strain energy release rate

Thus, the fracture stress is dependent on the modulus, the inherent flaw size and the critical strain energy, assuming conditions of plane stress. Smith[86] has shown that modulus increases with increasing volume fraction of filler. This would explain the observed increase in strength as filler content increases. Incorporation of silica particles into a resin increases the inherent flaw size, because of agglomeration of particles.[98] Thus, on the addition of the silica the flaw size C_0, may increase, causing the strength to fall compared to the strength of the unfilled resin.

It may be expected that the propensity for the formation of agglomerates to form, and hence the inherent flaw size, to increase with silica concentration. However, Lloyd[99] has reported that the inherent flaw size of various commercially available composites, with different filler particle sizes and concentrations, are similar. Similarity of inherent flaw size value may also explain why the strength increases as silica concentration increases, as one may have expected there to be larger agglomerates present as silica concentration increases giving a correspondingly larger inherent flaw size.

The relationship between G_{ic} and filler content is parabolic[100]. Since we have no knowledge of the silica content which corresponds to the maximum in G_{ic} it is impossible to predict the exact effect the silica content has on G_{ic}. However, as strength is increasing it may not be unreasonable to suggest that G_{ic} is also increasing with silica content up to 60%.

5.3.5 EFFECT OF SILICA CONCENTRATION OF YOUNG'S MODULUS IN BENDING

Several mathematical models have been derived to describe the relationship between the volume fraction of a filler in a composite and the modulus of the system[21]. Some models are more complex than others. For example, the "Reuss Model", (28), is a simplistic model because it does not account for effects due to the viscoelasticity of the matrix, filler packing efficiency, or filler shape and size. However, this model does give an indication of the effect of filler volume fraction on modulus (Figure 28).

$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{V_m}{E_m} \qquad (28)$$

Where E_c = Modulus of composite

E_f = Modulus of filler

E_m = Modulus of matrix

V_f = Volume fraction of filler

V_m = Volume fraction of matrix

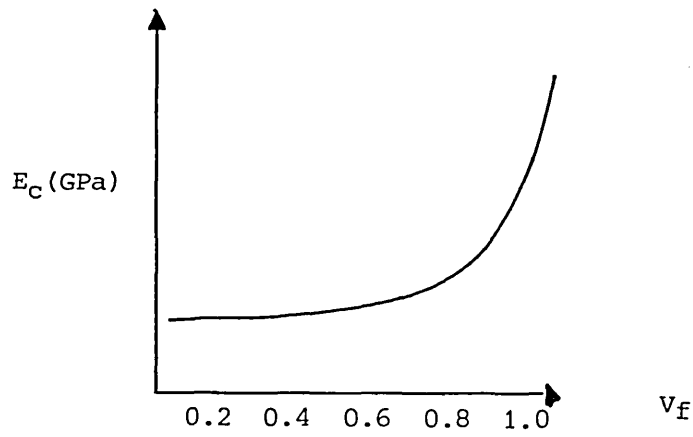


Figure 28 Effect of Filler Volume Fraction on Modulus

Neilsen and Lewis[101] have developed a model which attempts to predict the stiffness behaviour of a filled polymer using equation (29). The constant A takes into account the shape of the filler, the packing efficiency, and B compensates for the Poisson's ratio of the matrix. This model gives a more accurate value for the modulus of the composite, but the "Reuss Model" affords a reasonable prediction of the effect of filler volume fraction on modulus.

$$E_c/E_1 = \frac{1 + ABU_2}{1 - BXU_2} \qquad (29)$$

Where, $A = K_E - 1$. K_E = Einstein's coefficient = 2.5 for rigid spheres

$$B = \frac{E_2/E_1 - 1}{E_2/E_1 - A} \qquad (30)$$

$$X = 1 + U_2\left[1/U_{m2} - 1/U_m\right] \qquad (31)$$

E_c = Modulus of composite

E_1 = Modulus of matrix

E_2 = Modulus of filler

U_2 = Volume fraction of filler

U_m = Max. packing fraction of filler

Therefore, it was not wholly unexpected that the addition of silica should significantly increase the modulus and that increasing from volume fraction of 25% to 50% or 60% should also significantly increase the modulus. However as the "Reuss Model" predicts, the increase in modulus was not linear but a skewed increase in favour of higher volume fractions of filler. An interesting observation was that there was no significant difference between the moduli of the composites with a filler fraction of 50% and 60%. Clearly in this case the increased filler loading was insufficient to induce a significantly greater modulus. Referring to the "Reuss Model" this observation is not surprising as it is only beyond the 80% volume fraction of

filler that small increases in filler loading would be expected to significantly raise the modulus (Figure 28).

5.3.6 EFFECT OF SILICA CONCENTRATION ON SURFACE HARDNESS

The surface hardness of a composite is a function of resin type and state of the network with regards to degree of cure, time after cure, the concentration and type of filler.[102-107]

Results showed (Section 5.2.4) the incorporation of a harder phase into the resin increased hardness, and that as the concentration of the harder phase increased at the expense of the softer phase, so hardness increased. Similar results were observed by Li et al[85] using a light cured resin and borosilicate glass filler.

5.3.7 EFFECT OF SILICA CONCENTRATION ON VISCOELASTIC PROPERTIES

The dynamic mechanical properties of a composite are a function of the components in the system, their relative concentration and the nature of the interface between the two phases[37]. The storage modulus, measured at a frequency of 1 Hz and temperatures of 22 °C and 37°C, significantly increased with the addition of 25%, 50%, and 60% silica. Significant increases ($p \leq 0.05$) were also observed between the storage modulus of 25% and 50% and 25% and 60% filler levels. However, there was no significant difference ($p \leq 0.05$) between 50% and 60% silica.

An increase in storage moduli is observed, (Figures 24 to 26), because rigid silica particles are replacing softer resin. When the temperature was increased to 158°C there were greater differentials between the storage modulus of each formulation. This resulted in there being a more significant ($p \leq 0.01$) increase

in modulus as the silica concentration was increased from 0% to 25%, then 25% to 50%, and 50% to 60%. At lower temperatures, 37 °C, there was no significant difference ($p \leq 0.05$) between the storage modulus of the 50% and 60% silica.

These results show that the storage modulus of the composite resins depend on temperature and at high temperatures the composite with the 60% silica is the most rigid.

Previous workers [108-110] have shown that composites filled with inorganic fillers have a lower compressive creep rate than resin materials. It has also been observed that greater filler levels afford smaller creep rates [111]. Using tan δ at 37 °C as a gauge for the propensity to creep [43], it was found that replacement of the polymeric phase by an inorganic silica phase does significantly reduce ($p \leq 0.05$) the tan δ at 37 °C and so the creep rate would be expected to be less for the composites. There are also significant differences ($p \leq 0.05$) between the tan δ values of the composites with 25% and 50%, and 25% and 60% filler volume fraction. Therefore, addition of filler and increasing its concentration to 50% may afford reduced creep rates. The reduced creep rate is observed because the resin is replaced by inorganic silica. As the former has a greater propensity to flow than the latter, then any system which has more filler than resin will creep less - assuming the matrix and filler are identical in each formulation. No significant difference in tan δ is observed between 50% and 60% because insufficient resin has not been replaced by filler.

Addition of silica causes a fall in the alpha relaxation temperature, or Tg, at 1 Hz. A possible reason for this

observed reduction in Tg with increasing filler volume fraction, is that the solid filler particles behave as barriers which restrict the movement of growing chains and monomers[103]. This may result in a larger lower molecular weight fraction and pendant methacrylate groups being present, thus affording reduced Tg[110]. However, despite the alpha relaxation temperature of the resin being lowered, at the alpha relaxation temperatures the storage modulus of the composites was still greater than that of the unfilled resin; and so they will be more rigid, (see Figures 24 to 26). Also all the composites have lower tan δ values, (see Figures 21 to 23), and so they still have less of a propensity to flow and distort at higher temperatures.

5.4 CONCLUSIONS

5.4.1 EFFECT OF SILICA CONCENTRATIONS ON PROCESSING AND RHEOLOGY

Addition of 2 μm silica to a resin system alters the process requirement of the resin. Pre-milling and high and low shear mixing are required to ensure homogeneity of filler, good wetting of filler and proper dispersion of agglomerates. If insufficient shear forces are applied, the agglomerates are not dispersed and an inferior product is obtained. Incorporation of silica alters the rheological properties of the "dough". Substitution of PMMA with silica results in less polymer being available to interact with the monomer, thus, the composite resins behave more like viscous fluids and exhibit less elastic behaviour than the unfilled resins.

A consequence of the change in rheological properties is that these composite resins may only be successfully moulded at 175 °C by a compression moulding technique. Their propensity to flow is too large to allow these composites to be moulded by transfer or pseudo compression methods.

5.4.2 EFFECT OF SILICA CONCENTRATION ON THE MECHANICAL PROPERTIES OF THE COMPOSITE

In general, the mechanical properties of the polymer system are significantly increased ($p \leq 0.05$) if silica particles, which have an average particle size of 2 μm and have been coated with an organosilane coupling agent, are added to the resin in concentrations greater or equal to 25% by volume.

The mechanical property that is significantly reduced ($p \leq 0.05$) by addition of silica concentrations, greater or equal to 25% by volume is flexural strength. However, if the

silica concentration is increased to 60% (by volume) the reduction in strength when compared to the unfilled resin is less.

Increasing the filler volume fraction from 25% to 50% affords significant ($p \leq 0.05$) improvements in the mechanical properties, whereas increasing the filler volume fraction from 50% to 60% does not yield significant mechanical property enhancement - except in two cases: both surface hardness and the storage modulus at 158 °C are significantly increased ($p \leq 0.05$) if the silica volume fraction in the composite is raised from 50% to 60%. The 60% (by volume) silica reinforced composite is the optimum formulation as it affords superior mechanical properties. It combines higher stiffness, hardness, lower damping factor and thus creep rate, with the smallest sacrifice in strength.

Chapter 6: EVALUATION OF AN ORGANOZIRCONATE AS A POTENTIAL COUPLING AGENT FOR A DENTAL METHACRYLATE SYSTEM REINFORCED WITH SILICA

6.1 INTRODUCTION

It has been stated earlier, (Section 5.1.2), that a coupling agent must be present in a composite formulation if the optimum mechanical properties of the composite are to be realised.

The ability of a composite to transfer stress from the matrix phase to the filler phase, and vice-versa, is dependent on the quality of the interfacial bond[91]. For this reason several researchers[1,112] believe that to improve the mechanical properties of the composites, the bond between the interface of resin and filler must be improved. In an attempt to overcome the problems of adhesion between the organosilane and the filler, Turner et al[112] investigated the effect of adding 4-methacryloxyethyltrimellitic anhydride (4-META) to resins filled with unsilanated and silanated lithium aluminium silicate. They gauged the efficiency of cohesion between filler and matrix by measuring flexural strength and flexural modulus. Results showed that the 4-META improved the flexural strength significantly in the silanated filler only. Flexural modulus was unaffected. Thus, 4-META cannot be used as a direct substitute for organosilanes. Misra[113] investigated the use of zirconyl methacrylate as a possible coupling agent between calcium hydroxyapatite and a dental resin. The zirconium was in the +2 oxidation state and was only absorbed onto the surface of hydroxyapatite. The efficiency of the system was evaluated by comparison of diametral tensile strength. Results showed that the diametral tensile strength increased by 50% if the

hydroxyapatite was treated with the zirconyl methacrylate.

The objectives of this part of the research were to evaluate the effects of incorporating an organozirconate coupling agent, zironium in the +4 oxidation state in a microfilled composite resin, on the mechanical properties of the microfilled resin. The efficiency of the adhesion between the filler and the resin was judged by measuring flexural strength, viscoelastic properties, hardness, and abrasion resistance.

6.1.1 ADVANTAGES OF ORGANOZIRCONATE

It is claimed that organozirconates have many advantages over other organometallic coupling agents[114]. One advantage is that, when in an oxidation state of +4, zirconium accelerates peroxide initiator systems. Thus, the zirconate may act as a cure enhancer as well as a coupling agent.

Zirconates do not react with hindered amines, phenols, or nitrophenols. This is an important fact, as many dental systems contain an amine type cure accelerator, and no reaction may afford improved colour stability of the final resin. Another advantage of the organozirconate is that it is a rheology modifier. On reacting with the filler the organozirconate will change the silica from a hydrophilic to a more hydrophobic solid. As the resin is hydrophobic, a more hydrophobic filler is being dispersed in a hydrophobic resin. Increased compatability between solid and resin phases results in easier wetting of the solid by the resin[91] and therefore improved flow properties.

Improving the propensity for wetting of the solid by the resin will result in an increased critical pigment volume

concentration, ie that point in an inorganic-organic system at which just sufficient organic is present to occupy the voids between the inorganic particles. Coupling agents also protect the filler from hydrolytic degradation[115] by rendering it less hydrophilic. When silane coupling agents are added to the filler, the silane is first dissolved in water and is converted from the trialkoxy form to a triol, (Figure 29). The silane in the triol may either react with the silanol on the filler or react with the silanol group of another organosilane. Monomeric and oligomeric organosilanes are absorbed onto the surface of the filler. The organosilane may polymerise to form polysiloxanes. Lower molecular weight polysiloxanes may be washed away during preparation of the coated silica[116]. The silica is then dried with monomeric and oligomeric organosilane absorbed on the surface. However, the polysiloxane will still be present.

Organozirconates are not added to the filler in an aqueous solution, and are therefore still in the alkoxy form. The consequence of this is that they will not react with each other to form oligomers or polymers. The organozirconate is added to the monomer system and mixed with the filler. Diallyl ligands are substituted by the -Si-O- groups from the filler, however, the diallyl compound released from the reaction may polymerise during the cure reaction and join growing methacrylic polymer chains. Thus, the method of producing the bridge between resin and filler is more convenient using organozirconates as it is a one stage process during the cure and no residual molecules are left to contaminate the system.

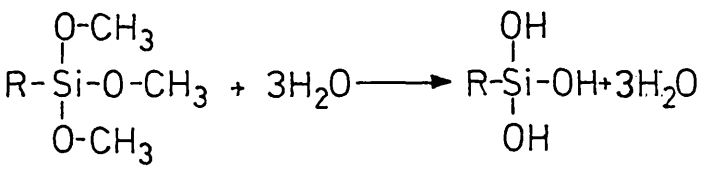


Figure 29 Hydrolysis of an Organosilane

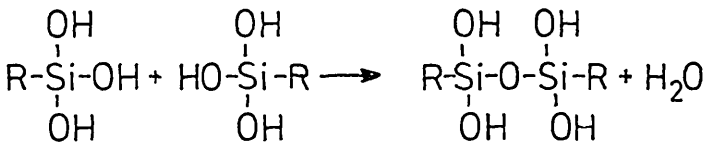


Figure 30 Step growth Polymerisation of an Organosilane

6.1.2 MECHANISMS OF COUPLING

Organozirconates, like organosilanes, are coupling agents which react with free protons on the surface of inorganic particles resulting in the formation of monomolecular layers which are organic in nature. The organic layer may then bond to the organic resin if the nature of their respective functionalities allows it. The inorganic filler used in this study was microfine silica, the average particle size being, approximately, 0.05 μm. Silica is the trivial name for silicon dioxide, SiO_2. There are several types of silica, some being more crystalline than others. Microfine silica fillers are amorphous. They contain five major types of bonds[117].

Si-O-Si- Siloxane

Si-O-H Silanol

Si-H Silane

Si-O-R or $Si-CH_2-R$ Organosilane

Amorphous silica is hydrophilic because of the presence of the silanol and silane bonds. The silanol is the functional group which reacts with the organozirconate resulting in a covalent bond between the coupling agent and the filler (Figure 31)

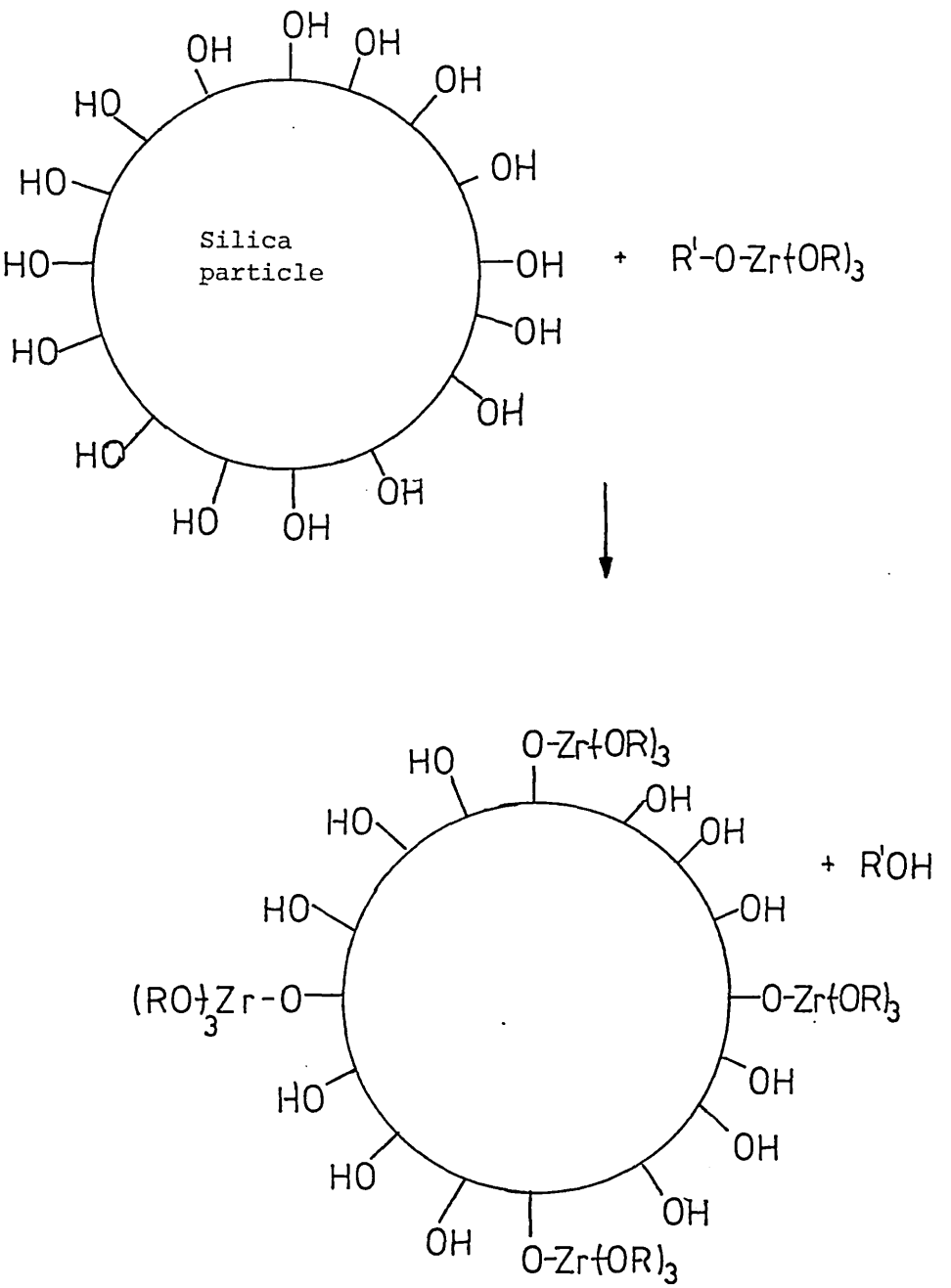


Figure 31 Reaction of Organozirconate and Filler Surface

The methacrylate ligands may join any growing polymer chain and create a bridge between the filler and the resin. (Figure 32).

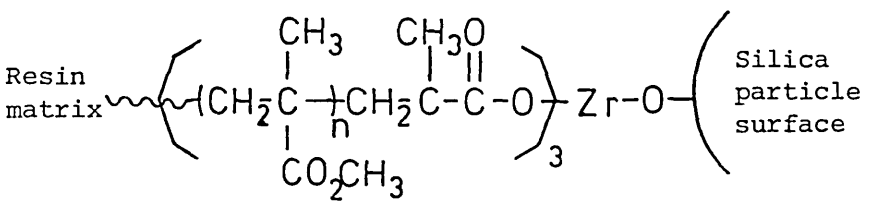


Figure 32 Interface between Resin and Filler using an Organozirconate Coupling Agent

6.2 EXPERIMENTAL AND RESULTS

6.2.1 INFLUENCE OF NEOPENTYL(DIALLYL)OXYTRIMETHACRYLZIRCONATE (NPDOMZ) CONCENTRATION ON THE PROCESSING AND RHEOLOGICAL PROPERTIES OF MICROFILLED TOOTH MATERIAL

(a) Preparation of Microfilled Composite Resins

Method

Each resin prepared had 60% volume of microfine silica particles whose average particle size was 50 nm*. However, due to the bulk density of the silica, this corresponded to a weight fraction of only approximately 20%. Five resins were prepared: which had the concentrations of 0%, 0.25%, 0.5%, 1% and 2.5% of the weight of NPDOMZ of the filler added. The resins were prepared in the same fashion as described in Section 5.2. However, prior to both the mixing and dispersion processes, all metallic and ceramic surfaces were washed with a dilute solution of NPDOMZ to eliminate the possibility of the coupling agent in the composite resin from reacting with these surfaces rather than the filler.

*Fillers obtained from DMG Gmbh, Hamburg, West Germany.

Results

As the NPDOMZ concentration was increased the mixing became easier. Less mixing time was required to achieve what appeared to be the same degree of wetting of the filler.

Difference in material viscosity of the resins was greatly marked at high shear rates, ie in the triple mill. The viscosity of the resins returned to a higher value at zero shear, although there was a recovery time - indicative of thixotropic behaviour.

(b) Rheological Properties

Method

The rheological parameters, G' and η', of each resin were determined after mixing in the same fashion as described in Section 2.2.10.

Concentration of NPDOMZ	η'(Pa.S) (min)	η'(Pa.S) (max)	G'(Pa) (min)	G'Pa) (max)
0%	*	*	*	*
0.25%	*	*	*	*
0.5%	217	93,780	2,879	14,120
1.0%	128	65,200	2,363	8,200
2.5%	39	23,630	1,223	3.564

*No values are reported for the 0% and 0.25% resins because of the inability to obtain reproducable data. This non-reproducibility is attributed to sample inhomogeneity.

(c) Compression Moulding of the Composite Resins

Method

The resins were moulded using the compression mould described in Section 5.2 using the following moulding conditions:

heat cycle	
pressure: temperature:	2 tons for 45 seconds, 4 tons for 3 minutes 15 seconds 175°C
cooling cycles	
pressure: temperature	4 tons 13°C

Each moulding was analysed for any defects or the presence of filler agglomeration. The samples were prepared for mechanical testing by removing any flash and polishing the faces using emery paper down to 200 grade.

Results

The resins were of suitable viscosity for moulding five days after mixing. Any attempted moulding before this time resulted in excess flashing of the material from the mould. Mouldings of the 0% and 0.25% resins all had large agglomerates of filler. On removal from the mould the mouldings of these two resins often fractured because the agglomerates acted as stress concentrators. The 0.5%, 1% and 2.5% resins gave mouldings which were free from any visible defects and agglomerates. The mouldings all appeared homogeneous and were easily removed from the mould. Mouldings of the 2.5% zirconate resin were slightly thinner than the 1% resins which were in turn thinner than the 0.5% resins.

6.2.2 INFLUENCE OF NEOPENTYL(DIALLYL)OXYTRIMETHACRYLZIRCONATE CONCENTRATION ON THE MECHANICAL PROPERTIES OF MICROFILLED COMPOSITE TOOTH MATERIAL

(a) Flexural Strength

Method

The flexural strength of each composite was determined as detailed in Section 4.2.2.

Results

Concentration of organozirconate. (w/w) filler concentration	Flexural Strength (MNm^{-2})	
	Mean	Standard Deviation
0.5%	55	11.0
1.0%	58	6.8
2.5%	76	6.6

Statistical analysis by Student's t test ($p \leqq 0.05$) (Appendix 4) showed:

(i) No significant difference between flexural strength of composite with 0.5% organozirconate and the composite with 1.0% organozirconate.

(ii) Significant increase, (38%), in flexural strength was seen if organozirconate is increased from 0.5% to 2.5%.

(iii) Significant increase in flexural strength, (31%), if the organozirconate concentration is increased from 1% to 2.5%.

(b) Modulus in Bending

Method

The modulus of elasticity in bending was derived using the load-deflection curve obtained in the analysis of flexural strength. A tangent was drawn to the steepest initial portion of the load deflection curve. The modulus of elasticity in bending, E_B, is given by:

$$E = \frac{L^3 M}{4bd^3} \quad (27)$$

where L = length of support (m)
M = gradient of tangent (N/m)
b = Sample breadth (m)
d = Sample depth (m)

Results

Concentration of organozirconate. (w/w) filler concentration	Modulus in Bending (GPa)	
	Mean	Standard Deviation
0.5%	3.556	1.500
1.0%	4.137	0.967
2.5%	6.500	0.578

Statistical analysis by Mann-Whitney - U - test (Appendix 9) showed:

(i) No difference between the moduli of the 0.5% and 1.0% organozirconate composites.

(ii) No difference between the moduli of the 2.5% organozirconate composite.

(c) Surface Hardness

Method

Surface hardness was determined as described in Section 3.2.5.

Results

Concentration of organozirconate (w/w by filler concentration)	Surface Hardness Shore D durometer	
	Mean	Standard Deviation
0.5%	91	0.707
1.0%	91	0.707
2.5%	91	0.632

Statistical analysis by Student's t-test ($p \leq 0.05$) (Appendix 4) indicated no significant difference between the surface hardness of any composites produced.

(d) Viscoelastic Properties

Method

The Viscoelastic properties were determined as outlined in Section 3.2.6.

Results

Concentration of organozirconate (w/w filler concentration)	Storage modulus E' at 37°C (GPa)	Damping factor tan δ at 37°C	Alpha relaxation temperature, Tg (°C)	Storage modulus E' at 158°C (GPa)
0.5%	2.965 (SD=.191)	0.0495 (SD=1.4x10)	116	.239 (SD=0.0175)
1.0%	2.805 (SD=.134)	0.0505 (SD=7x10)	116	.221 (SD=0.0215)
2.5%	2.813 (SD=.250)	0.0520 (SD=1.4x10)	118	.222 (SD=0.0134)

Statistical analysis by the Student's t-test (Appendix 4) showed:

(a) There was no difference in viscoelastic properties for any of the composites with organozirconate coupling agent.

(b) All composites had significantly greater E'_{37} and E'_{157} than the unfilled resin. The tan δ_{37} was significantly less than the unfilled resin and there was a fall in Tg.

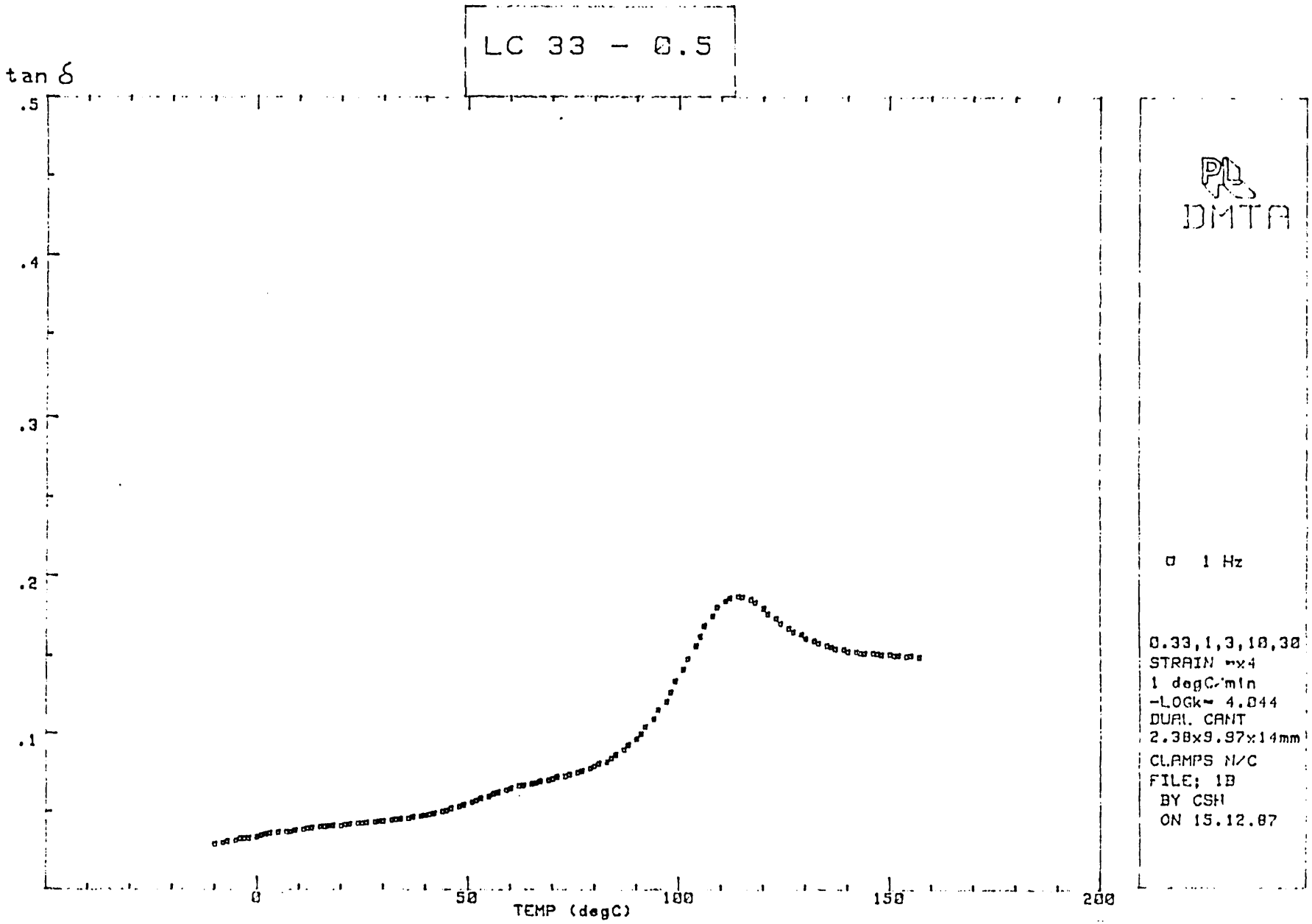


Figure 32 tan δ V's Temperature for 0.5% NPDOMZ

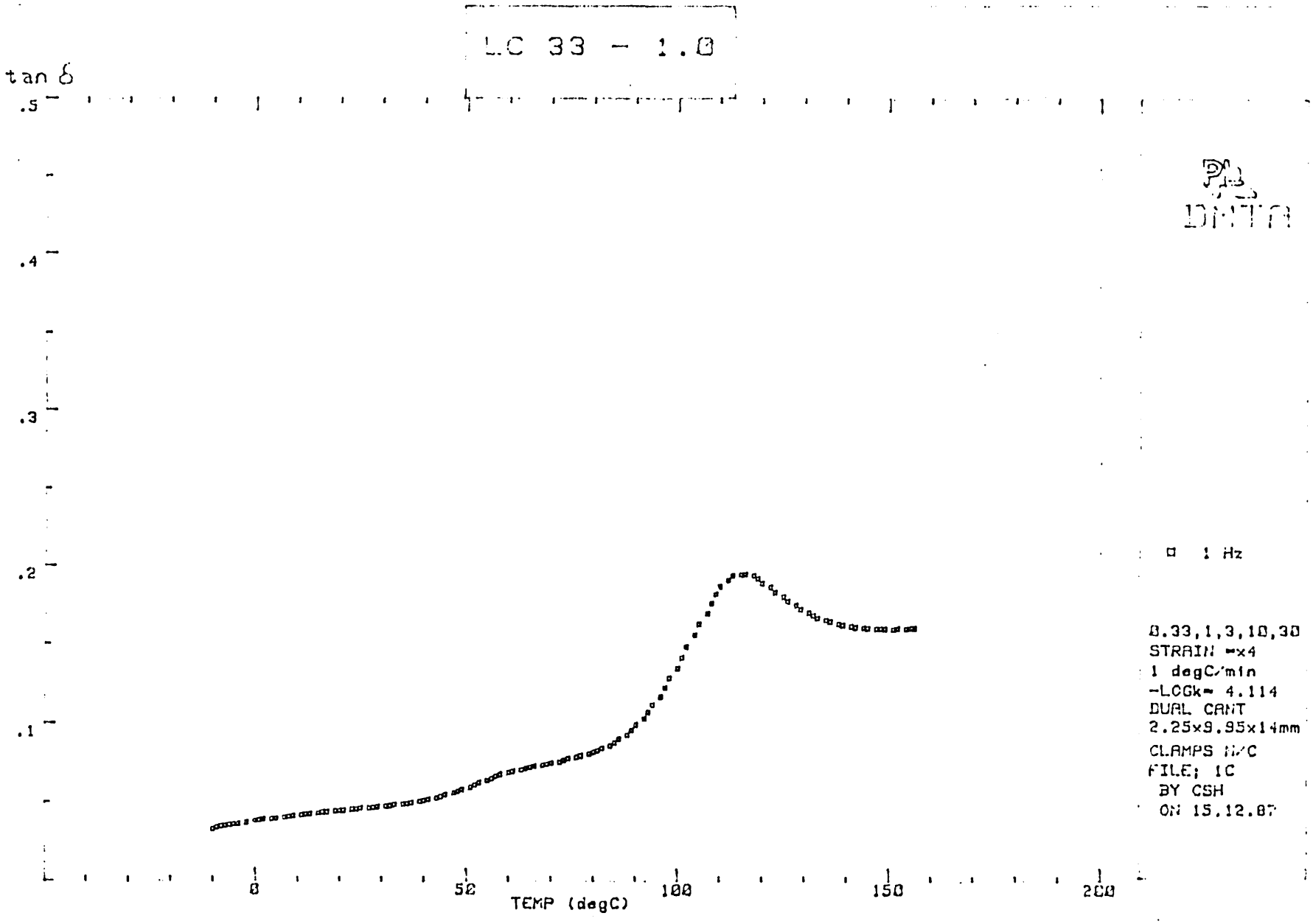


Figure 33 tan δ V's Temperature for 1.0% NPDOMZ

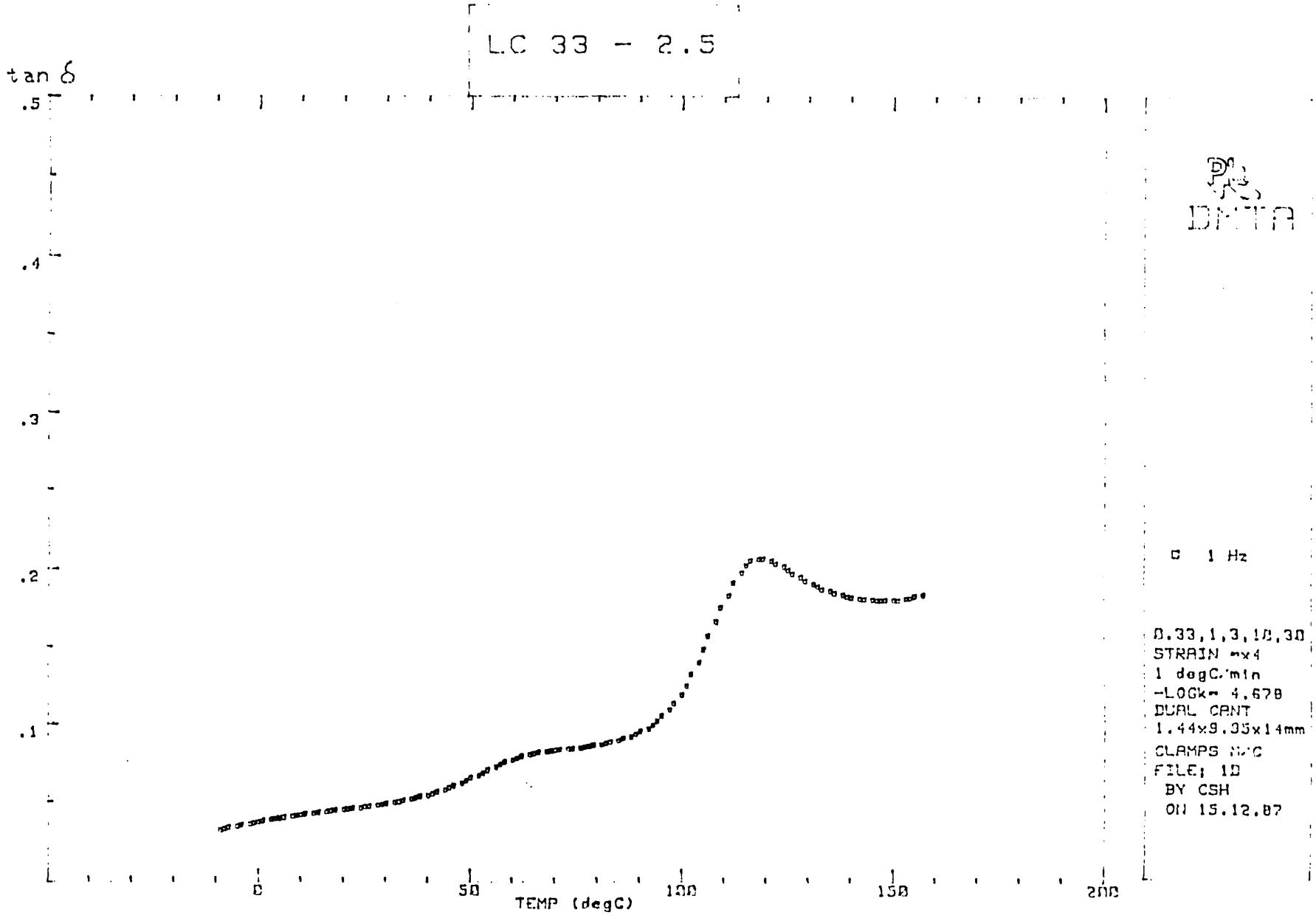


Figure 34 tan δ V's Temperature for 2.5% NPDOMZ

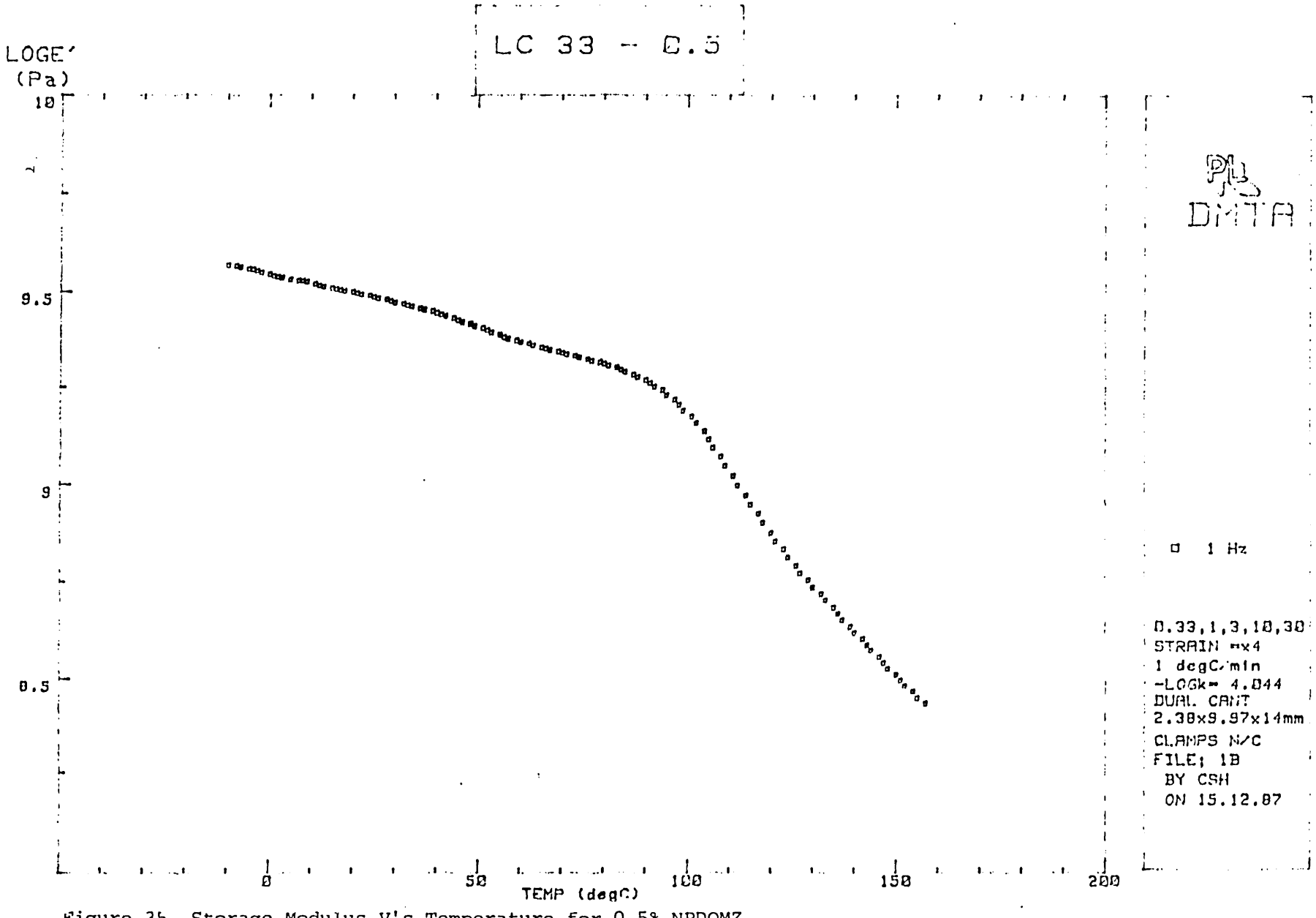


Figure 35 Storage Modulus V's Temperature for 0.5% NPDOMZ

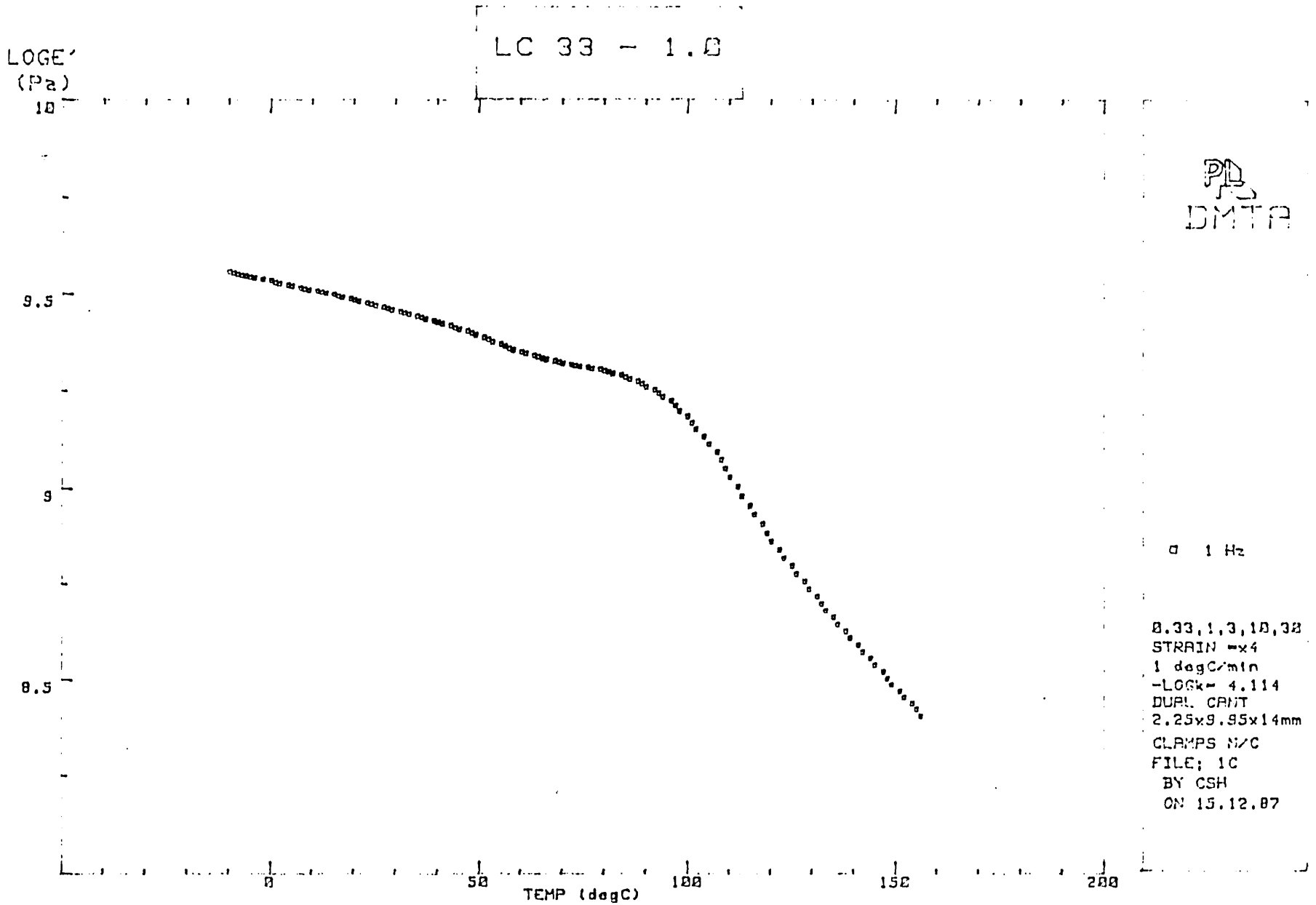


Figure 36 Storage Modulus V's Temperature for 1.0% NPDOMZ

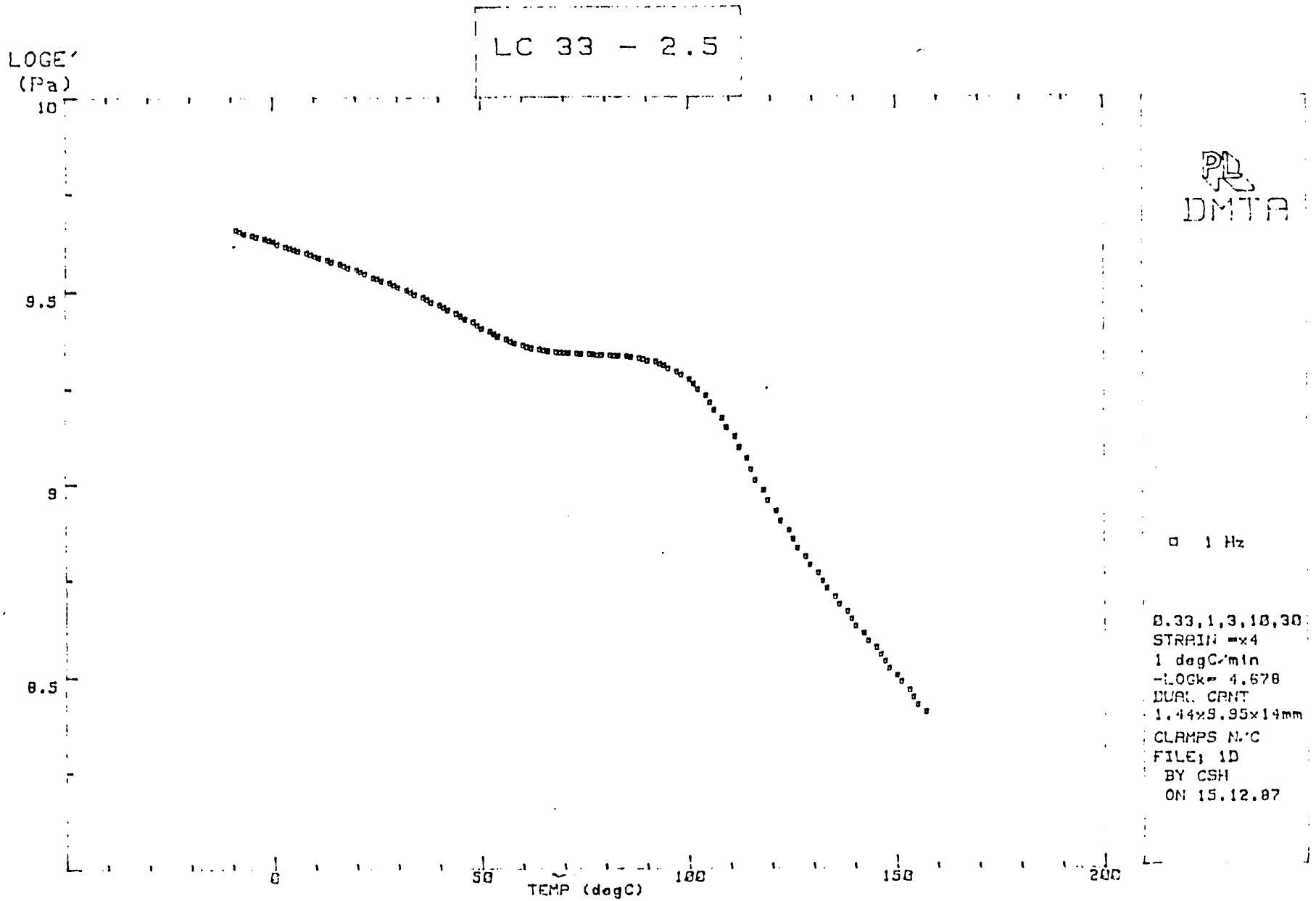


Figure 37 Log Storage Modulus V's Temperature for 2.5% NPDOMZ

6.3 DISCUSSION

6.3.1 INFLUENCE OF ORGANOZIRCONATE CONCENTRATION ON THE PROCESSING AND RHEOLOGY OF THE COMPOSITE TOOTH MATERIAL

(a) Mixing and Dispersion of the Filler in the Resin Matrix

The mixing and dispersion of the composites became easier as the concentration of the organozirconate was increased. This signifies that the solid filler phase and liquid monomeric phases are more compatible as the concentration of coupling agent is increased. A higher coupling agent concentration in the filler resin will result in more of the hydrophilic silanol groups on the filler surface being converted to -Si-O-Zr-O-R type bonds which are less hydrophilic. As the liquid phase is hydrophobic, a less hydrophilic filler will be more compatable with the liquid phase and will afford easier mixing and dispersion.

(b) Rheological Properties

All of the filled resins are shear thinning. As the frequency of deformation is increased the viscosity of the resin decreases. This is in agreement with findings of previous workers[96,97]. It was noted that after passing the materials through a triple mill the resins did not return to their initial viscosity immediately after the application of shear ceased, but there was a recovery time - indicative of thixotropic materials. Comparison of the dynamic viscosity and dynamic real shear modulus clearly shows that increasing the organozirconate concentration reduces the dynamic

viscosity and dynamic shear modulus over the frequency range 0.01 Hz to 10 Hz. Increasing the organozirconate concentration from 0.5% of filler weight reduces the dynamic viscosity by, on average, 78%. The dynamic shear modulus is also reduced by, on average, 67%. Thus, increasing the concentration of organozirconate in the formula alters the viscoelastic properties of the composite by increasing the viscous component and reducing the elastic behaviour of its flow properties.

These observations explain the improved mixing and dispersion characteristics during preparation of the resin because it is easier to mix and disperse a filler if the filler is easily wetted and the liquid is less viscous.[91]

(c) Compression Moulding of Microfilled Resins

After mixing, the resins were too fluid to mould so they were allowed to increase in viscosity and elasticity with time. The doughing of the material is identical to that for the filled resins coated with an organosilane. The material becomes more viscous as the PMMA molecules first dissolve, then disentangle in the monomers present[39]. After five days at room temperature, the resins had the required viscosity and rigidity to allow them to be moulded without excess material leaking from the mould. The homogeneity of the moulded test pieces indicated the compatability of the liquid and solid phases. The 0% and 0.25% organozirconate composite had visible agglomerates of filler. This observation signifies poor wetting and,

therefore, poor compatability between the solid and liquid phase[91]. Agglomerates of filler will behave as stress concentrators[91], this explains the observation that most of the samples fractured when they were being removed from the mould. The samples of the other formulations were much more robust despite being of a thinner section in some cases. The 0.5%, 1% and 2.5% organozirconate formulation appeared to be homogeneous (by visual inspection). At these levels of coupling agent there was sufficient compatability between phases to ensure wetting and breakdown of large agglomerates. The average thickness of the test pieces produced, reduced from 2.5 mm to 1.34 mm as the concentration of organozirconate increased from 0.5% to 2.5% The difference in thickness is due to the 2.5% resin being more fluid and less rigid after five days than the 0.5% resin.

6.3.2 INFLUENCE OF ORGANOZIRCONATE CONCENTRATION ON THE MECHANICAL PROPERTIES OF MICROFILLED TOOTH POLYMER

(a) Flexural Strength

Increasing the organozirconate concentration to 2.5% of filler weight significantly improved flexural strength. The observed increase in flexural strength may be a result of the following mechanisms:

(i) Reduced hydrophilicity

By increasing the concentration of coupling agent to 2.5%, more silanol groups on the filler surface are replaced by the less hydrophilic -Si-O-Zr-O-R groups. This renders the filler more compatible with the

hydrophobic resin. Increased compatibility will give the resin a greater propensity to wet the filler[91]. If the filler particles are not completely wetted either air or impurities will be entrained at the interface. The air or impurities will behave as stress concentrators manifesting in a catastrophic failure of the composite.

The tendency for the fillers to agglomerate will also be reduced by improved compatibility between the resin and filler phases. If agglomerates are present these should increase the inherent flaw size of the material, thus reducing flexural strength.

(ii) Increased covalent bonding

Increasing the number of organozirconate molecules will increase the number of potential reaction sites for the resin on the filler surface. Improvement of the adhesion between the resin and filler due to a greater number of covalent bonds between the two phases will result in an improved flexural strength.

Smith[87] has reported the average flexural strength for microfilled composites lies between 60 MPa and 80 MPa. Only the 2.5% NPDOMZ concentration compared favourably with these composites. Thus, a 2.5% concentration of NPDOMZ is required to generate an interfacial bond which will create a composite which has strength comparable to best commercial microfilled composites[87].

(b) Modulus of Elasticity in Bending

The modulus of elasticity in bending was only significantly increased if the NPDOMZ concentration was increased to 2.5% w/w of filler. This follows the same trend as the flexural strength. Therefore, it is postulated that at 0.5% and 1% NPDOMZ concentrations, there is poorer adhesion or bonding between the matrix and filler. The reasons for the inferior coupling at the 0.5% and 1% NPDOMZ may be poorer wetting of the filler by the resin and reduced covalent bonding between the filler and resin, (as discussed in Section 6.3.2). The moduli of the composites produced with the 0.5% and 1% NPDOMZ lie inside the values 3 - 4 GPa stated by Smith[87] for microfilled composites. However, as the modulus in bending for the unfilled resin is 3.68 GPa, there does not appear to be any advantage in filling the resin with these formulations if modulus is to be increased.

At the 2.5% NPDOMZ level, the modulus in bending was increased to 6.5 GPa, which is greater than the values for the commercially available composites. Although this cannot at this stage be wholly attributed to superior interfacial bonding, it does illustrate that the organozirconate coupling agent can produce a composite resulting in improved mechanical properties.

(c) Surface Hardness

Altering the organozirconate coupling agent concentration had no effect on the surface hardness of the composite.

Watts et al[30] have reported that the surface hardness of a composite will reflect the degree of cure in the resin

if the type and volume of filler is kept constant. It may, therefore, be assumed that as the hardness values are constant for all organozirconate concentrations, then the degree of cure must be the same. This leads to the conclusion that increasing the organozirconate concentration from 0.5% to 2.5% weight of filler does not increase the cure of the resin phase.

(d) Viscoelastic Properties

Statistical analysis showed that there was no difference in the viscoelastic properties of the composites regardless of NPDOMZ concentration. The viscoelastic properties are dependent on the filler loading level and type, and the interfacial bond[37]. These results appear to conflict with the data from the modulus and flexural strength experiments. The viscoelastic properties suggest there may either be no difference between the interfacial bonds created by the different level of coupling agent, or that there is no difference in the filler/filler, or filler/polymer friction[118]. These results can, therefore, not be taken as conclusive because it is conceivable that due to poor wetting, a low coupling agent concentration will afford a composite with large agglomerates. Thus, due to poor bonding between the resin and filler, tan δ will be high. However, if a higher concentration of coupling agent is used, this may afford improved wetting and better dispersion. This may result in greater filler/polymer friction, thus increasing tan δ. This theoretical scenario illustrates how viscoelastic

properties in different polymer composites may be similar due to different structural effects. Even the storage modulus at 158 °C did not significantly change with increasing NPDOMZ concentration. It may be argued that the storage modulus will be most sensitive to the filler volume fraction as was seen in Section 5.2.5, and so no difference is observed.

Therefore, in order to conclusively prove whether increasing the zirconate concentration to 2.5% w/w filler concentration effectively increases the filler/matrix bond, a study of the surface chemistry between the coupling agent and the filler and matrix phases must be carried out.

6.4 CONCLUSIONS

The organozirconate coupling agent, NPDOMZ, behaves as a rheology modifier. If the concentration of NPDOMZ is increased, the resulting composite will have a lower viscosity. If insufficient NPDOMZ is added to a composite system with a volume fraction of 60% 0.05μm silica, then the filler will not be dispersed effectively, affording agglomeration of filler particles.

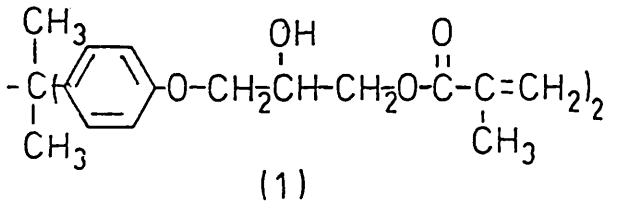
The flexural strength and modulus in bending are significantly improved ($p \leq 0.05$) if the NPDOMZ concentration is increased to 2.5% w/w of the filler. The surface hardness and viscoelastic properties do not appear to be significantly affected ($p \leq 0.05$) by the NPDOMZ concentration.

Based on the modification of the rheological properties of the composite, and on the criteria of modulus of elasticity and flexural strength, used by other workers studying coupling agents[112,113] it may be concluded that increasing the NPDOMZ concentration to 2.5% w/w filler increases the filler/resin bond by physical and/or chemical effects.

Chapter 7: DEVELOPMENT OF A NOVEL DENTAL MONOMER

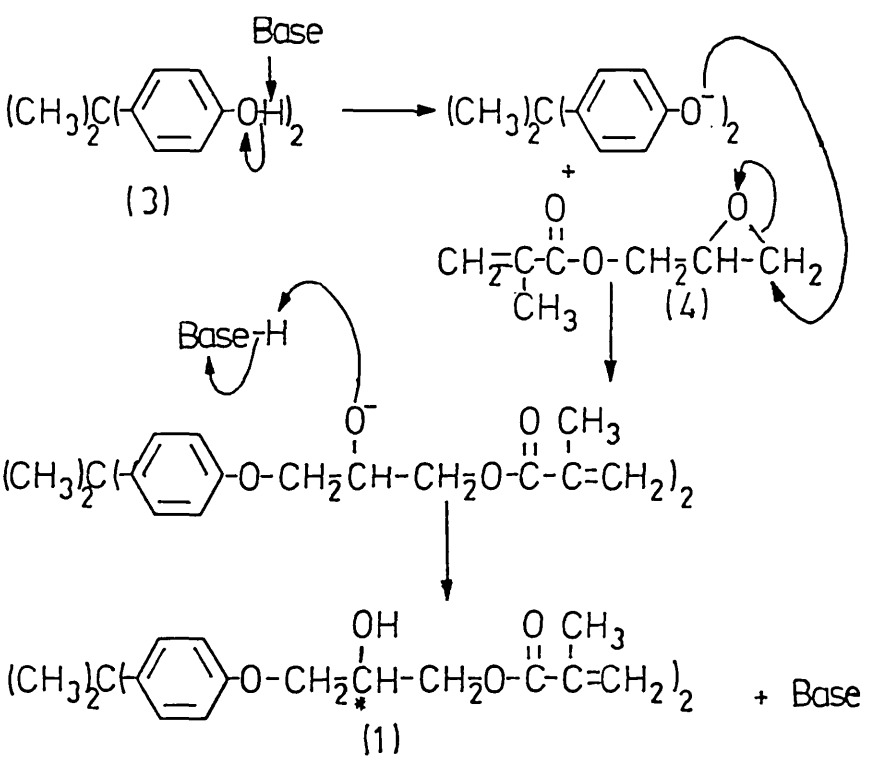
7.1 INTRODUCTION

The aim of this section of the thesis was to produce a derivative of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]propane, BisGMA (1), which might have superior mechanical and rheological properties to BisGMA.



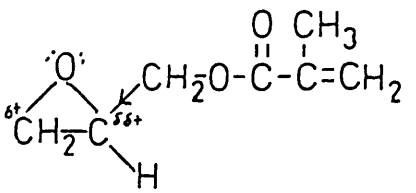
(1)

BisGMA is the reaction product of Bisphenol A (3) and glycidyl methacrylate (4). Two or more moles of (4) are added to one mole of (3) with 0.5 - 1.0 percent of a tertiary amine, for example dimethyl p-toluidine, as base catalyst. The yield from this reaction is increased when it is carried out at 60°C under nitrogen. (Scheme 1)



Scheme 1

Branched and straight chain isomers are formed due to the possibility of the substitution reaction occurring at the primary or secondary carbon of the oxirane ring. The bis-anion of Bisphenol A attacks the primary carbon rather than the secondary carbon because of two effects: steric hindrance due to the ester group attached to secondary carbon, and also, because there will be a slight positive inductive effect towards the secondary carbon rendering it less electropositive than the primary carbon.



(4)

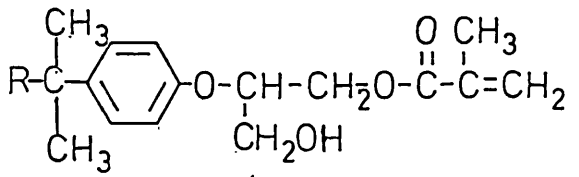
BisGMA was patented for use in dentistry as a restorative material in 1962[55]. Several criticisms of the resin have been made, despite the fact that it did show improved mechanical properties compared to materials previously used[87]. These criticisms include:

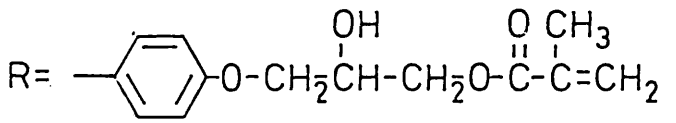
1) High viscosity - A diluent monomer such as triethyleneglycol dimethacrylate must be added to BisGMA to achieve reasonable working properties. The addition of a diluent monomer increased the shrinkage of the polymerisation

and possibly reduced the mechanical properties[87].

2) Water absorption[119] - The resin is hydrophilic due to the presence of polar alcohol functional groups. Absorption of water leads to reduced mechanical properties and dimensional stability[87].

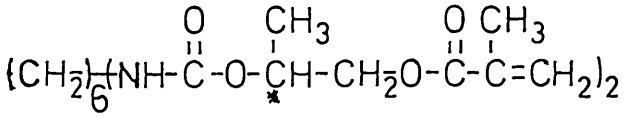
3) Purity - BisGMA possesses two chiral centres; therefore, four diastereoisomers of BisGMA must exist and so there is no one pure form[120]. Ruyter[121] has isolated two structural isomers of BisGMA from commercial BisGMA. One isomer is straight chain (1), the other, a branched chain form (2). These isomers were isolated in a ratio of 3:1 in favour of the straight chain. As there are two structural isomers each with two chiral centres then eight diastreoisomers must exist.





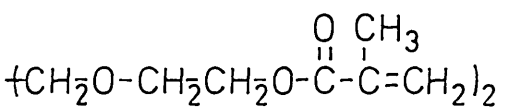
All of the problems associated with BisGMA are created by the secondary alcohol group. This group hydrogen bonds to other BisGMA molecules which then increases the viscosity of the resin. The alcohol functional group is hydrophilic and will also hydrogen bond to water increasing the propensity for water absorption.

Removal of the secondary alcohol group will reduce these problems and several workers have already achieved this to yield alternative monomers.



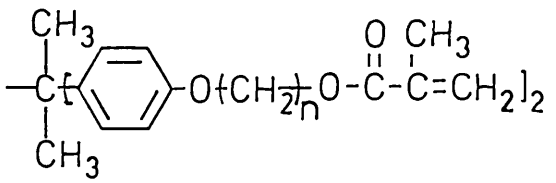
(5)

1,6-[bis-diaminocarboxyloxy(2-propylmethacryloyloxy)] hexane



(6)

Triethylene glycol dimethacrylate

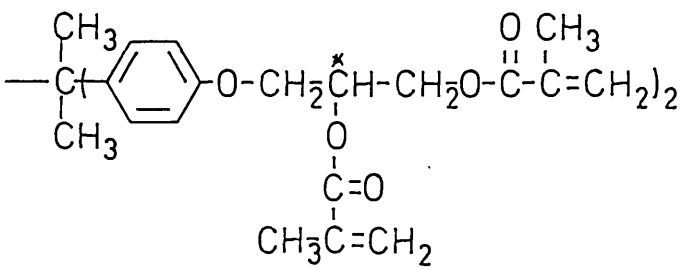


(7)

n=2:2,2-bis-[p-(2-methacryloyloxyethoxy)phenyl] propane

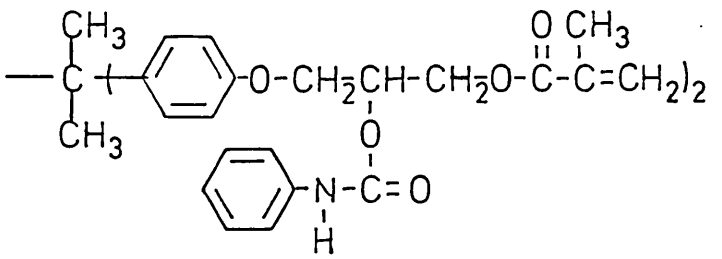
(8)

n=3:2,2-bis-[p-(3-methacryloyloxypropoxy)phenyl] propane



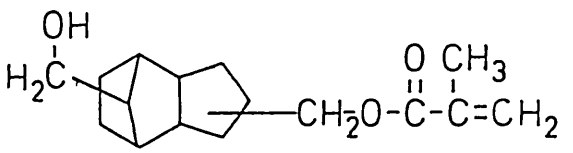
(9)

2,2-bis-[p-(2-methacryloyloxy-3-methacryloyloxypropoxy)phenyl] propane



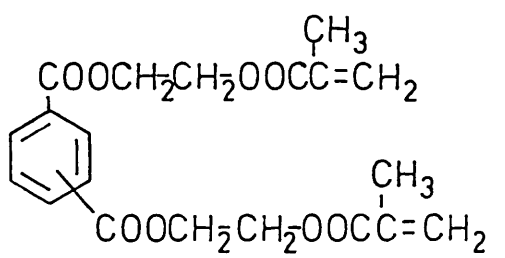
(10)

2,2-bis-[p-(2-phenylcarbamoyloxy-3-methacryloyloxypropoxy) phenyl]propane



(13)

Bis(methacryloyl)tricyclo (5.2.1o.^{2,6}) decane

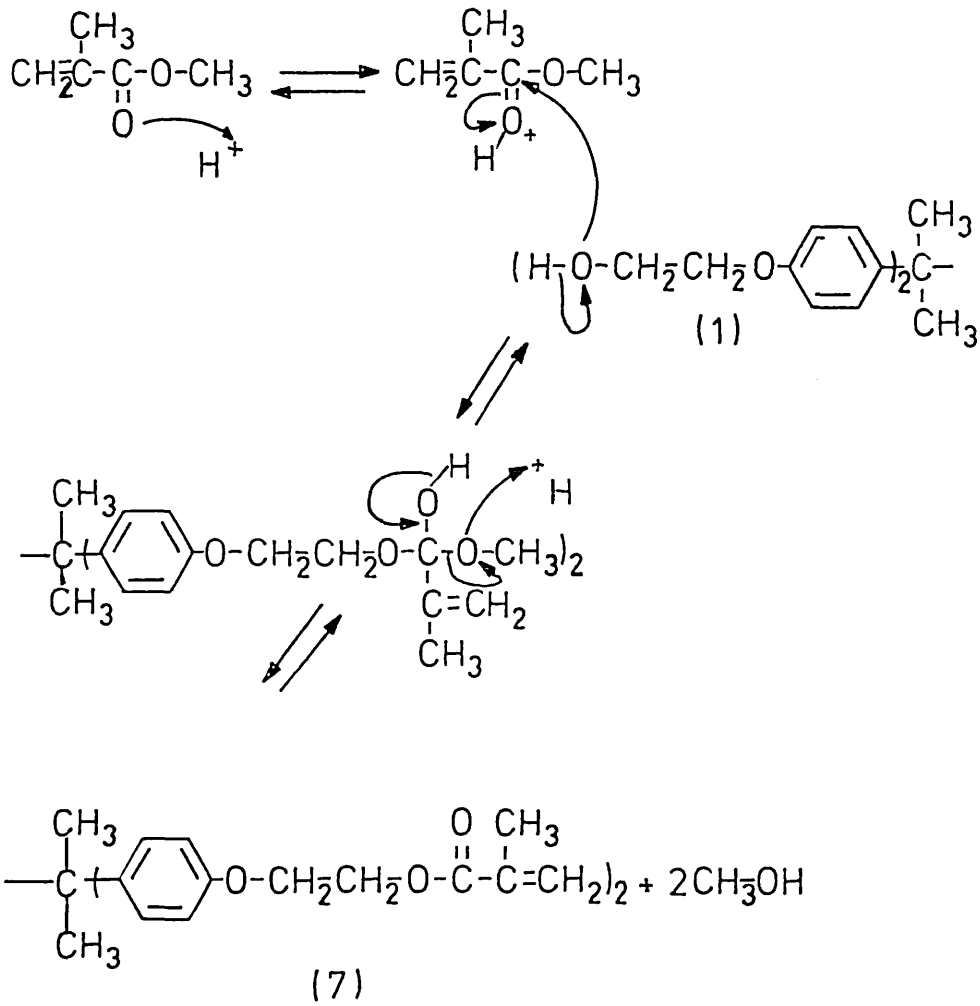


(16)

Di-methacryloyloxyethylphthalates

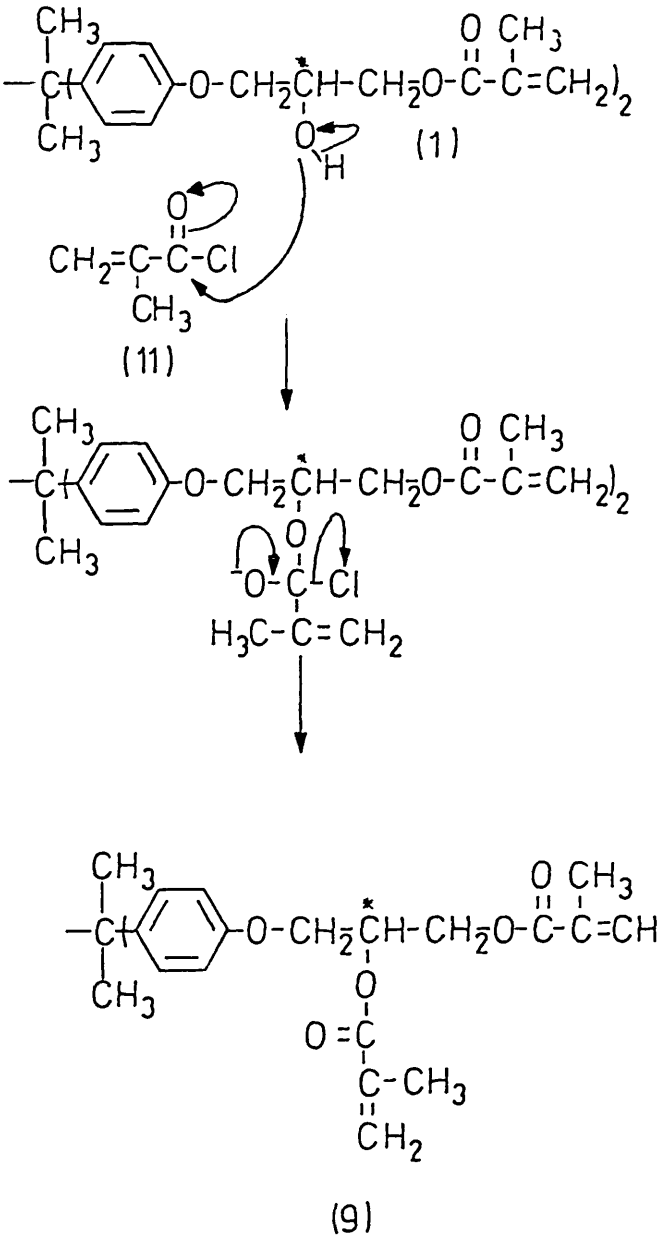
Compounds (9) and (10) can be considered to be derivatives of (1).

The methacrylates 2,2-bis-(p-(β-hydroxyethoxy)phenyl)propane dimethacrylate (7) and 2,2-bis(p-β-hydroxypropoxy)phenyl)propane dimethacrylate (8) are both produced by the acid or base catalysed transesterification reaction of methyl methacrylate and 2,2-bis (p-(β-hydroxyethoxy(phenyl)propane or 2,2-bis-(p-(β-hydroxy propoxy)phenyl)propane respectively. Both (7) and (8) do not possess chiral carbons or alcohol groups. This reduces the problems of water absorption, high viscosity and purity. Interestingly both of these compounds were isolated as crystalline solids.[122] (See Scheme 2)



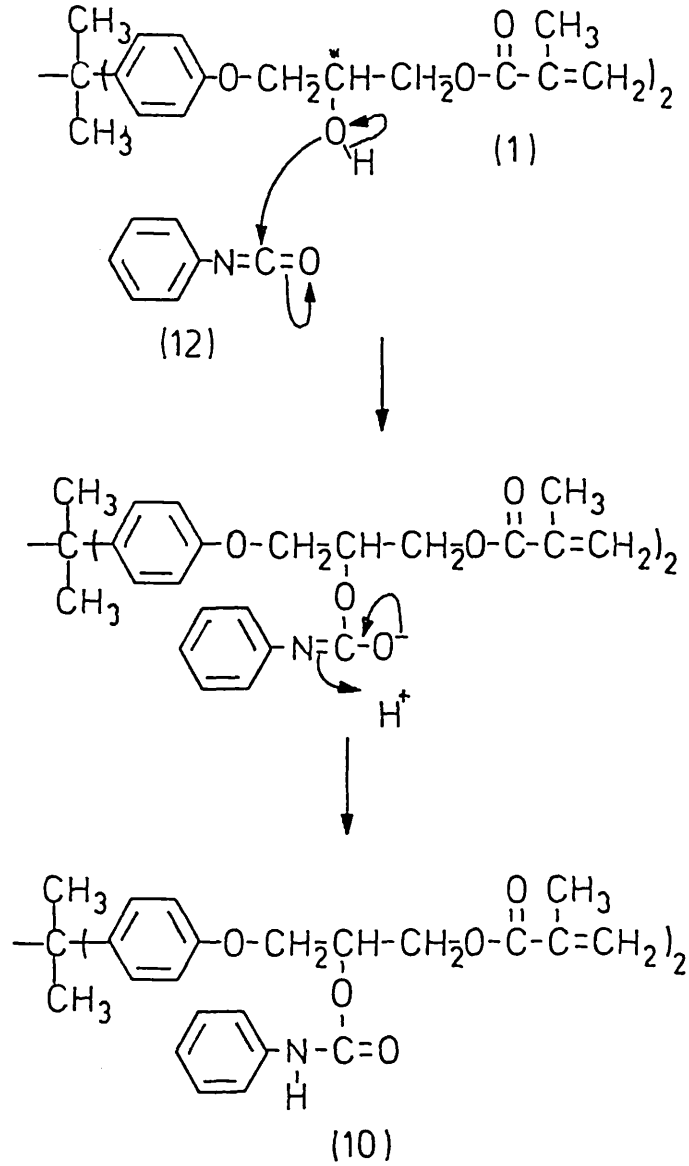
Scheme 2 Mechanism for Synthesis of 7

Esterification of BisGMA (1) with methacryloylchloride (11) in the same fashion as described above yields (9). This reaction has transformed the alcohol group into an ester which reduces the water absorption and viscosity because of the decrease in hydrogen bonding [123]. However, there remains the problem of having two chiral centres present and purity must still be questioned. (Scheme 3)



Scheme 3 Synthesis of 9

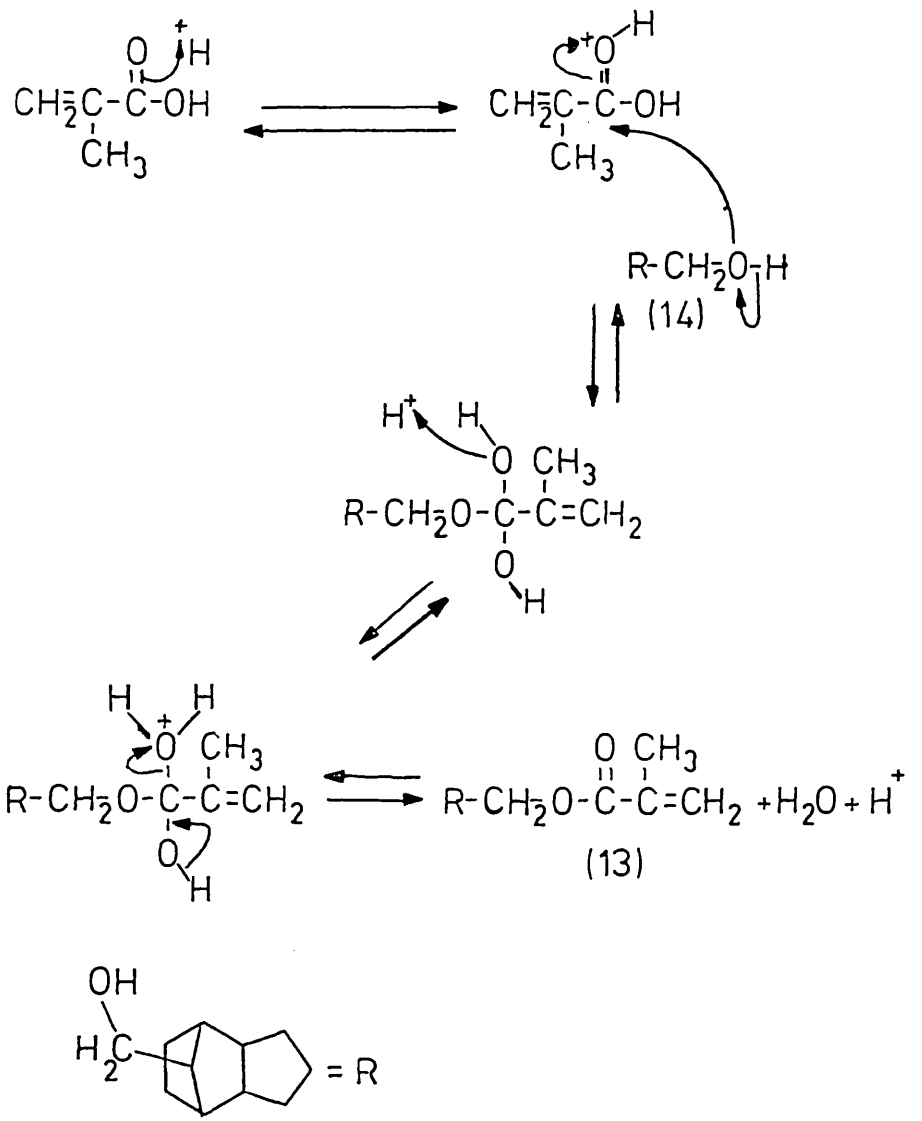
The alcohol attached to the chiral carbon on (1) has also been reacted with an isocyanate affording a urethane[124] such as (10). The methacrylate (10) is the product of the addition reaction between (1) and phenyl isocyanate (12) but it too offers similar advantages and disadvantages shown by the ester (9). (Scheme 4)



Scheme 4 Synthesis of 10

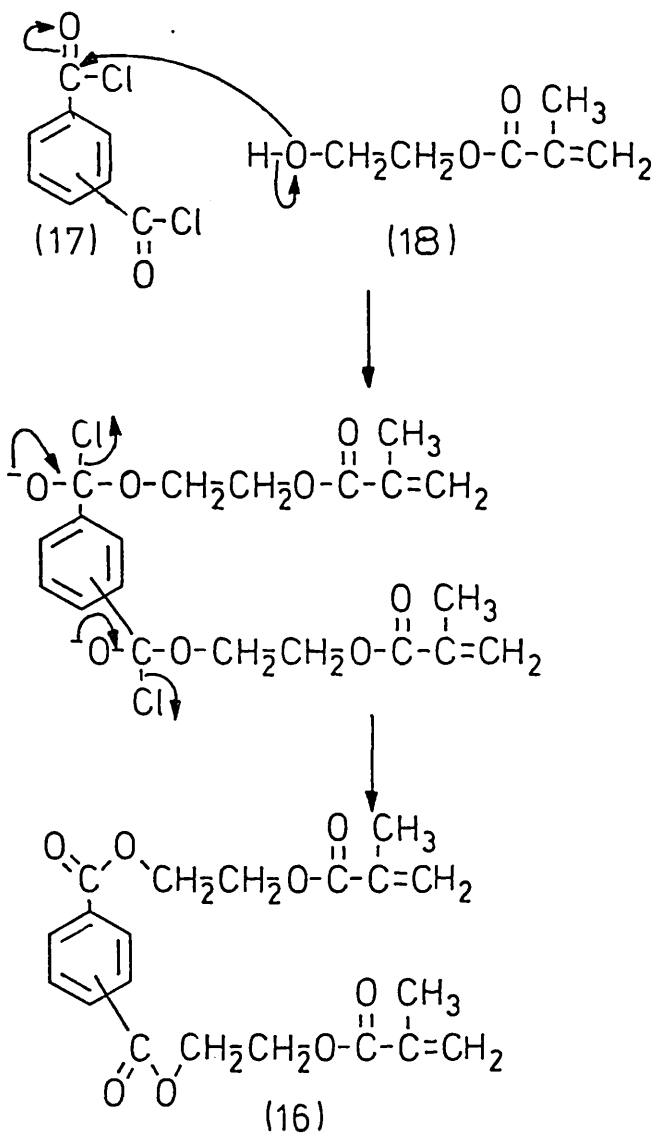
Bis (methacryloyl)tricyclo (5.2.1.$O^{2,6}$) decane (13) is a dimethacrylate which does not possess chiral centres, secondary alcohols, or aromatic rings. The cyclic alkyl structure gives rigidity to the derived polymer chain[125] which is necessary to give a high modulus polymer; a pre-requisite for a filling material.

The monomer (13) is prepared by reacting dihydroxymethyltricyclo (5.2.1.$O^{2,6}$) decane (14) with methacrylic acid in the presence of an acid catalyst. (Scheme 5)



Scheme 5 Synthesis of 13

In an attempt to overcome the problem associated with (1) Bowen[126] devised a ternary liquid eutectic system of workable viscosity containing aromatic diester dimethacrylates (16). These methacrylates are crystalline until they are mixed at which point they form a liquid. These aryl diester dimethacrylates are synthesised by reacting a benzene dicarboxylic acid chloride (17) with a hydroxylated methacrylate ester (18). It is claimed that such monomer eutectics produce excellent composite and sealant materials[120]. (Scheme 6)



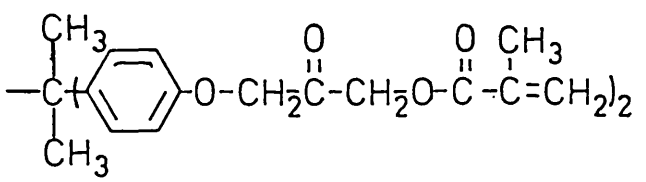
Scheme 6

In their attempts to overcome the problems associated with BisGMA previous workers have either modified the secondary alcohol group or devised a novel system based on other molecules, for example (5) and (6).

The disadvantages of BisGMA are only partly resolved if on modification of the alcohol the chiral centres remain, because the derivative produced will have four diastereoisomeric forms.

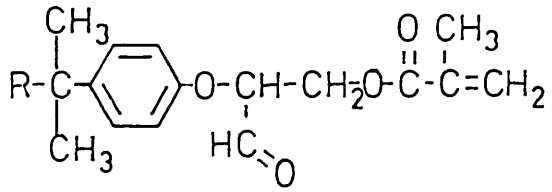
It appeared logical that if the secondary alcohol was modified to a ketone via oxidation this step would remove the problem of secondary bonding and the derivative would be achiral, ie have no stereoisomers.

Commercial BisGMA contains two isomeric structures - straight (1) and branched chains (2). The straight chain possesses two secondary alcohol functionalities which upon oxidation will afford the diketone (17).



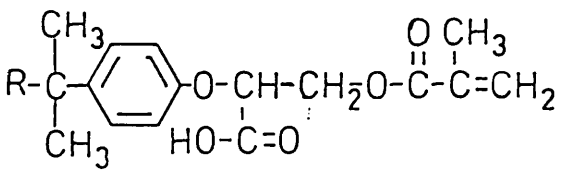
(17)

The branched chain form contains a primary and a secondary alcohol group. Oxidation of this isomer of BisGMA should yield a compound which contains a ketone and an aldehyde (18).

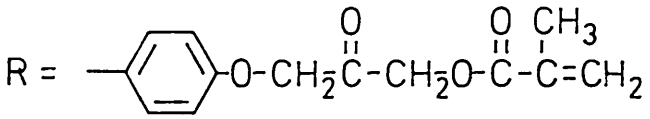


(18)

The aldehyde may be further oxidised to a carboxylic acid (19)



(19)



The ratio of straight chain BisGMA to branched in commercial BisGMA is 3:1[121]. Thus, in an oxidation of commercial BisGMA the major product should be the diketone (17).

Several reagents may be used to oxidise alcohols to their carbonyl derivatives. The oxidation of BisGMA is complicated by the possibility of polymerisation of the methacrylic double bond by either ionic or free-radical polymerisation[127]. There is also the possibility of addition to the methacrylic double bond, or hydrolysis of the ester part of the molecule. Several oxidation reactions were studied in an attempt to obtain pure (17) in a high yield.

7.2 RESULTS AND DISCUSSION

7.2.1 OXIDATION OF BisGMA WITH JONES REAGENT

When BisGMA (1) was treated with Jones Reagent[128] (2.2 equivalents of Cr (VI) for every OH) in an acetone solution not exceeding 30 °C the resultant reaction mixture was found (tlc) to contain a complex mixture of products along with some starting material. The appearance of a green inorganic solid confirmed that the chromium had been reduced from an oxidation state of VI to III.

Refluxing the reaction mixture resulted in the complete reaction of the starting material and tlc analysis indicated the presence of two compounds plus baseline material. The baseline material probably contained the acid derivative (19). The complex nmr spectrum of this material indicated the presence of a carboxylic (COOH) proton at 11δ and did not possess the alcohol OH proton. The material was a dark brown solid which had a sharp smell. The structure was assigned as (19) (33%). The two compounds which appeared above the baseline were separated by column chromatography. The first homogeneous product obtained was a pale yellow oil and was identified as the diketone of BisGMA (17) (26%). The nmr spectrum had no alcohol OH and analytical data indicated the structure assigned as (17).

The second homogeneous product was an orange/yellow oil. The nmr spectrum obtained was very complex and as yet no structure has been assigned but a possible structure is (18).

On refluxing, the BisGMA was totally consumed, however this was accompanied by an increased amount of baseline material on tlc. The chromic acid may be polymerising the monomer by cationic polymerisation of the methacrylic double bond, or forming complex decomposition products. This would account for the low yield which theoretically should be much higher.

7.2.2 OXIDIATION OF BisGMA WITH PYRIDINIUM CHLOROCHROMATE

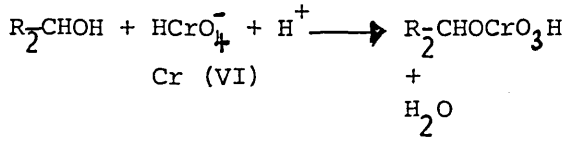
It has been reported[129] that alkanols which possess acid labile groups may be oxidised to corresponding carbonyl compounds without affecting the acid labile group by use of pyridinium chlorochromate. This was of interest as BisGMA (1) possesses an ester group which may be susceptible to acid hydrolysis. The reaction of (1) with pyrindinium chlorochromate (6 equivalents) in refluxing dichloromethane afforded three products. The carboxylic acid (19) (30%) of the branched BisGMA (2) was isolated along with the diketone of BisGMA (17) (29%) and some of a third compound, a yellow/orange oil, the structure of which has not been assigned unequivocally but its nmr spectrum matched the spectrum of the yellow/orange product obtained from the oxidation of (1) using Jones reagent.

The products of the reaction were coloured, and on analysis by tlc this colour remained on the baseline - indicative of chromium by-products or decomposition products. The yields of (17) and (19) are very similar to the yields in the Jones oxidation of (1).

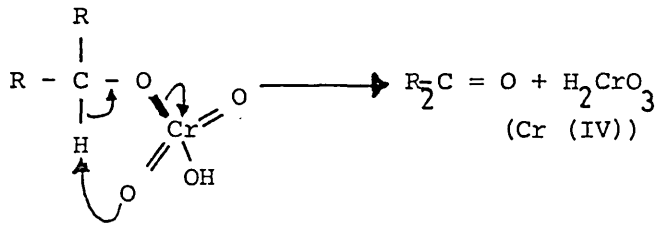
It appears that the reaction conditions are too severe and that the presence of chromiums ions and possibly the acidic environment led to low yields through cationic polymerisation yielding oligomers or complex decomposition products.

Scheme 7 Oxidation of Secondary alkanols by Chromium VI [130]

(a) Formation of chromate ester



(b)



(c) $R_2CHOH + Cr\ (IV) \longrightarrow R_2COH + Cr\ (III)$

(d) $R_2COH + Cr\ (IV) \longrightarrow R_2C = O + Cr\ (V)$

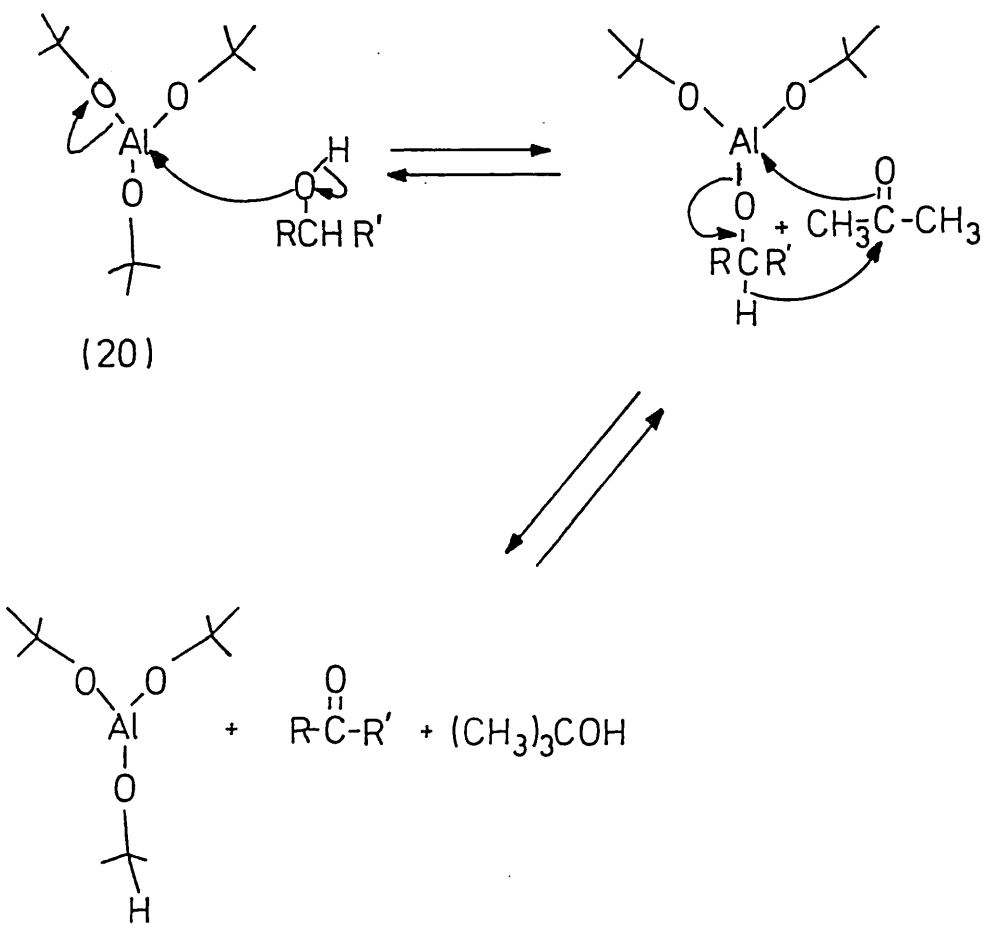
(e) $R_2CHOH + Cr\ (V)\ ester \longrightarrow R_2C = O + Cr\ (III)$

In step (b) deprotonation of the ester occurs giving the ketone and chromium (IV). Chromium (IV) is reduced to chromium (III) by forming an enol in step (c). The enol is oxidised to an alkanol by chromium (VI) affording chromium (V). Finally, the chromium (V) is reduced to chromium (III) by oxidation of the alkanone, via a chromate ester.

7.2.3 ATTEMPTED OPPENAUER OXIDATION of BisGMA (1)

The use of aluminium tertiary butoxide (20) for oxidation of alcohols to yield carbonyl compounds is recommended for those molecules which possess other reactive groups such as double bonds [131,132].

In an attempt to reduce the formation of by-products and polymeric products obtained in previous methods the reaction of (1) and aluminium tertiary butoxide was studied. The Oppenauer oxidation proceeds as shown in Scheme 10 and is an equilibrium reaction. Thus the reaction yield will be dependent on the nucleophilic strength of the alcohol.



Scheme 8

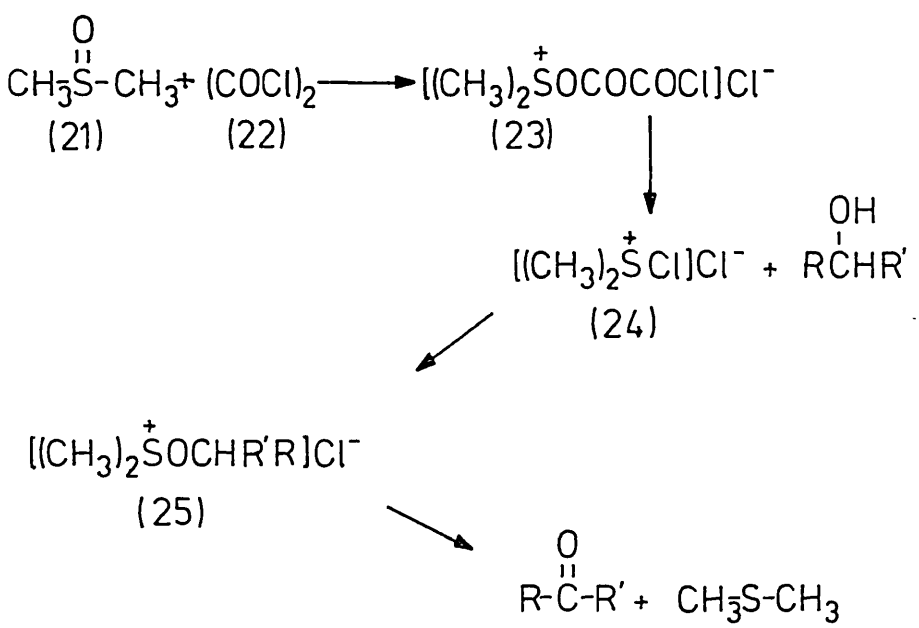
Tlc analysis indicated no trace of reaction after stirring for 24 hours at room temperature. Heating at reflux for 8 hours also resulted in no reaction (by tlc). This lack of reaction is attributed to the poor nucleophilic strength of the alcohol thereby reducing its propensity to attack the aluminium.

7.2.4 ATTEMPTED OXIDATION OF BisGMA WITH ALUMINIUM ISOPROPOXIDE

A variation of the Oppenauer oxidation[132] is the use of aluminium isopropoxide with cyclohexanone as solvent[133]. This method apparently has two advantages over the normal Oppenauer oxidation. The isopropoxide makes the aluminium more electrophilic and thus more susceptible to nucleophilic attack by the OH on BisGMA. Cyclohexanone boils at a higher temperature than acetone and thus affords a higher reaction temperature (110°C as opposed to 56°C). The reaction mixture was stirred for eight hours at room temperature followed by stirring for six hours at 110°C. Tlc analysis (of the reaction mixture) showed the presence of starting materials only. Thus, despite making the aluminium more electrophilic the alcohol functional groups of the BisGMA still did not appear to have sufficient nucleophilic strength to attack the aluminium isopropoxide.

7.2.5 OXIDATION OF BisGMA BY "ACTIVATED" DIMETHYLSULPHOXIDE

The oxidation of alkanols with dimethylsulphoxide (DMSO) activated by oxalyl chloride (22) has been reported by Swern and Omura[134,135]. The reaction is carried out at low temperatures (-65°C) and under mild conditions. The reaction (1) with the dimethylsulphoxide/oxalyl chloride afforded three products which were separated by column chromatography. The first product was dimethylsulphide. The second product, a yellow oil, was identified as diketone (1.25g, 75%). The third product was a yellow/orange oil. The possible structure of this product from consideration of the analytical data is (18). The oxidation reaction proceeds as shown in Scheme 11. The "activated" DMSO intermediate (23) forms dimethyl chlorosulphonium chloride (24) which is transformed to the dimethylalkoxy sulphonium salt (25) which upon reaction with a base, typically triethylamine, produces dimethylsulphide and the carbonyl product.[135] (Scheme 9)



Scheme 9

This method of synthesis of (17) was found to be the most satisfactory with regard to yield of products as it did not appear to form complex by-products or polymers. Another advantage is that the time required for the reaction is only three hours. The only impracticality associated with this method is the temperature control. The temperature must remain below -10°C because above this value an explosive reaction occurs between (21) and (22). The oxidising efficiency of (24) is also reduced at elevated temperatures due to diminishing stability of the species.[135]

The yellow resin produced was not readily soluble in methyl methacrylate or other common solvents such as ether, dichloromethane, or toluene. (In addition, the amorphous resin did not form a crystalline solid). Suspicions about the purity of the oxidation product must be raised due to the fact that the material only formed an amorphous solid and not crystals. Also, the solid was insoluble in common solvents, such as: ether, ethyl acetate, dichloromethane and methyl methacrylate. If the solid was pure one would have expected it to be soluble in these solvents.

7.2.6 EFFECT OF REPLACING BisGMA WITH THE DIKETONE OF BisGMA, BisGMAO, ON THE MECHANICAL PROPERTIES OF A TOOTH RESIN FORMULATION

Statistical analysis of the results showed that there was no difference in the flexural strengths, Young's modulus or surface hardness of the polymerised BisGMA or the polymerised BisGMAO materials. Both polymers had similar Tg, δ , and tan at 37 ℃. Thus, as the mechanical properties were the same, changing the functionality of the BisGMA molecule from a diol to a diketone did not significantly affect the structure of the glassy state network. However, there were differences observed in the viscoelastic properties of the materials in the rubbery state above Tg. At the onset of the alpha relaxation the value of tan δ of the BisGMAO was higher than the tan δ of the BisGMA. Also, the storage modulus of the BisGMA was greater than the storage modulus of BisGMAO in the rubbery state. This storage modulus above Tg is indicative of the degree of crosslinking in a polymer.[36] Thus the BisGMA system appears to be more crosslinked than the BisGMAO. This may be because the BisGMAO had oligomerised, during its preparation, affording a smaller concentration of dimethacrylate molecules available for crosslinking the system.

7.3 EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 397 infrared spectrophotometer, and H nmr spectra with a JEOL JNM PMX 60 SX NMR spectrometer, using tetramethylsilane as internal reference in an appropriate solvent. Reactions were monitored by tlc on Merck DC-Alufolien Kieselgel 60 F 254 with light petroleum-ethyl acetate as solvent. Column chromatographic separations were achieved by pressurised short-path columns with Keiselgel H (Nach Stahl) type 60 as absorbent. Solvents were reagent grade.

Developments Reagents For Thin Layer Chromatography

The following methods were used:

(a) Ultraviolet irradiation of tlc plates impregnated with a fluorescent indicator was routinely employed.

(b) Iodine vapour was a general, but indiscriminating reagent.

(c) A 0.5% aqueous potassium permanganate solution.

7.3.1 REACTION OF BisGMA (1) WITH JONES REAGENT

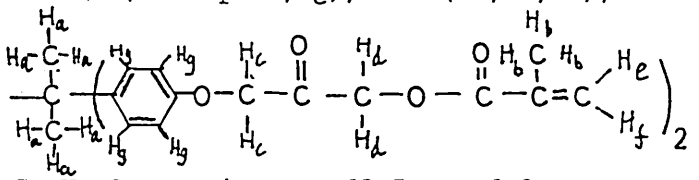
(a) Preparation of Jones Reagent

Chromium trioxide (26.72 g, 0.2672 moles) was added to concentrated sulphuric acid (23 mls) and a brown slurry formed. When the solid had dissolved in the acid the solution was made up to 100 mls with distilled water.

(b) Oxidation Reaction

BisGMA (7.28 g, 14.3mmoles) was dissolved in acetone (50 mls). Jones reagent (36 mls, 96.2mmoles of Cr^{7+}) was carefully added and the reaction was left stirring overnight. The reaction mixture was then extracted with ethyl acetate which was then washed with water, saturated

aqueous sodium bicarbonate and brine, dried (Mg SO) and evaporated in vacuo to give a dark brown oil which was chromatographed on silica gel to give two pure products. The first isolated product was BisGMAO (17) as a yellow oil (1.5g, 26%). λ (max) 3010, 3020 (aromatic =C-H stretch, alkene =C-H stretch), 2990, 2980, (aliphatic C-H stretch), 1740 (C=O stretch), 1600, 1500 (aromatic skeletal vibrations), 1240 - 1220, (aryl-alkyl and C-O-stretch), 1180 (C-O stretch) and 825 cm^{-1} (1,4-disubstituted aromatic deformations. δ ($CDCl_3$) (1.44(6H,s,H_a), 1.75(6H,s,H_b), 4.40(4H,s,H_c), 4.75(4H,s,Ha), 5.35(2H,multiplet,H_c), 5.75(2H,bs,Hf), and 6.7(8H,q,H_g)



$C_{29}H_{32}O_8$ requires C, 68.50; H,6.30%
Found C, 68.50; H,6.30%.
The second products has not yet been identified.

The aqueous sodium bicarbonate washings were acidified with dilute hydrochloric acid and extracted with ethyl acetate. The ethyl acetate was washed with water and brine; dried ($MgSO_4$); and evaporated in vacuo to give a dark brown oil which was chromatographed on silica gel to give (19) (0.6g, 33%) as a dark brown oil. λ(max) 3400-2500 (broadδ-OH for $-CO_2H$), 2975, 2925 (alphatic C-H stretch), 1740-1720 (broad C=O stretch), 1600, 1500 (aromatic skeletal vibrations), 1240-1220 cm^{-1} (Aryl-Alkyl C-O str), 1180 (C-O str), and 825 cm^{-1} (1,4-disubstituted aromatic).

7.3.2 REACTION OF BisGMA (1) WITH PYRIDINIUM CHLOROCHROMATE

BisGMA (9.4g, 18.46mmoles) was dissolved in dichloromethane (500 mls) and pyridinium chlorochromate (18g, 83.5mmoles) was added carefully and the reaction was left stirring overnight. The reaction mixture was diluted with ether (600 mls) and the precipitated solid (chromium salts) were filtered then washed with ether. The combined organic phases were washed with water, brine, saturated sodium bicarbonate solution and brine; dried ($MgSO_4$); and evaporated *in vacuo* to give a brown oil which was chromatographed on silica gel to give three pure components. The first compound isolated was (17) (1.75 g 24%). The second product has, as yet, not been identified. The final material was unreacted (1) (1g, 10.5%).

7.3.3 ATTEMPTED OXIDATION OF BisGMA USING ALUMINIUM TERTIARY-BUTOXIDE

BisGMA (2.4g, 4.7mmoles) was dissolved in dry acetone (15 mls) and toluene (15 mls). Aluminium t-butoxide (1.15g, 4.7mmoles) dissolved in dry toluene (15 mls) was added to the above solution and allowed to stir overnight at room temperature. Tlc showed no reaction had occurred.

In an attempt to promote a reaction the mixture was refluxed for a further 8 hours. Analysis of the reaction mixture showed no reaction had occurred.

7.3.4 ATTEMPTED OXIDATION OF BisGMA WITH ALUMINIUM ISOPROPOXIDE

BisGMA (2.2g, 4.3mmoles) was dissolved in cyclohexanone (10 mls) and toluene (40 mls) was added along with aluminium isopropoxide (1g, 4.9mmoles in toluene, 15 mls).

The reaction mixture was stirred overnight but this did not afford any reaction. The reaction mixture was then refluxed for 8 hours but this had no effect and no products were detected.

7.3.5 OXIDATION OF BisGMA BY "ACTIVATED" DIMETHYL SULPHOXIDE (DMSO)

Oxalyl chloride (0.96 mls, 11mmoles) was dissolved in dichloromethane (5 mls) and cooled to -65°C. DMSO (2.0 mls, 24mmoles) in dichloromethane (5 mls) was added to the oxalyl chloride over 5 minutes and then stirred for 10 minutes.

BisGMA (2.5g, 4.9mmoles) in dichloromethane (10 mls) was added to the reaction mixture over 5 minutes and then stirred for 5 minutes. Triethylamine (5g, 50mmoles) was added cautiously and the mixture was allowed to rise to room temperature. The reaction mixture was added to 1,1,1,-trichloroethane (250 mls) and then washed with water, dilute hydrochloric acid, water, brine, saturated aqueous sodium bicarbonate solution, water, brine; dried ($MgSO_4$), and evaporated *in vacuo* to give a yellow brown oil which was chromatographed on silica to give two products. The first product, a yellow oil, was identified as (17) (1,31g, 75%). The second product has not yet been identified (0.19g, 7.6%).

7.3.6 BULK POLYMERISATION OF A DOUGH FORMULATION INCORPORATING BisGMAO AND BisGMA

Preparation of BisGMAO dough		Preparation of BisGMA dough	
Component	Weight percent	Component	Weight percent
BisGMAO	11%	BisGMA	11%
MMA	22%	MMA	22%
EGDMA	5.5%	EGDMA	5.5%
Benzoyl peroxide	2%	Benzoyl peroxide	2%
PMMA	59.5%	PMMA	59.5%

The Benzoyl peroxide was dissolved in the MMA and EGDMA and BisGMAO was added to the resulting mixture. Any solid material that did not dissolve was powdered with a mortar and pestle. The PMMA was added and the material mixed in an orbital mixer followed by a triple mill until a homogeneous mix was achieved. The dough was matured for 120 minutes by which time it had appropriate flow properties to facilitate transfer moulding. The materials were moulded for 4 minutes at 175 °C at a pressure of 4 tons. The moulded test pieces were tested for:

flexural strength (method outlined in 4.2.3);

Young's modulus (method outlined 3.2.4);

viscoelastic properties (method outlined in 3.2.6);

surface hardness (method outlined in 3.2.5).

This procedure was repeated for the BisGMA dough and the mechanical properties of the two materials were compared.

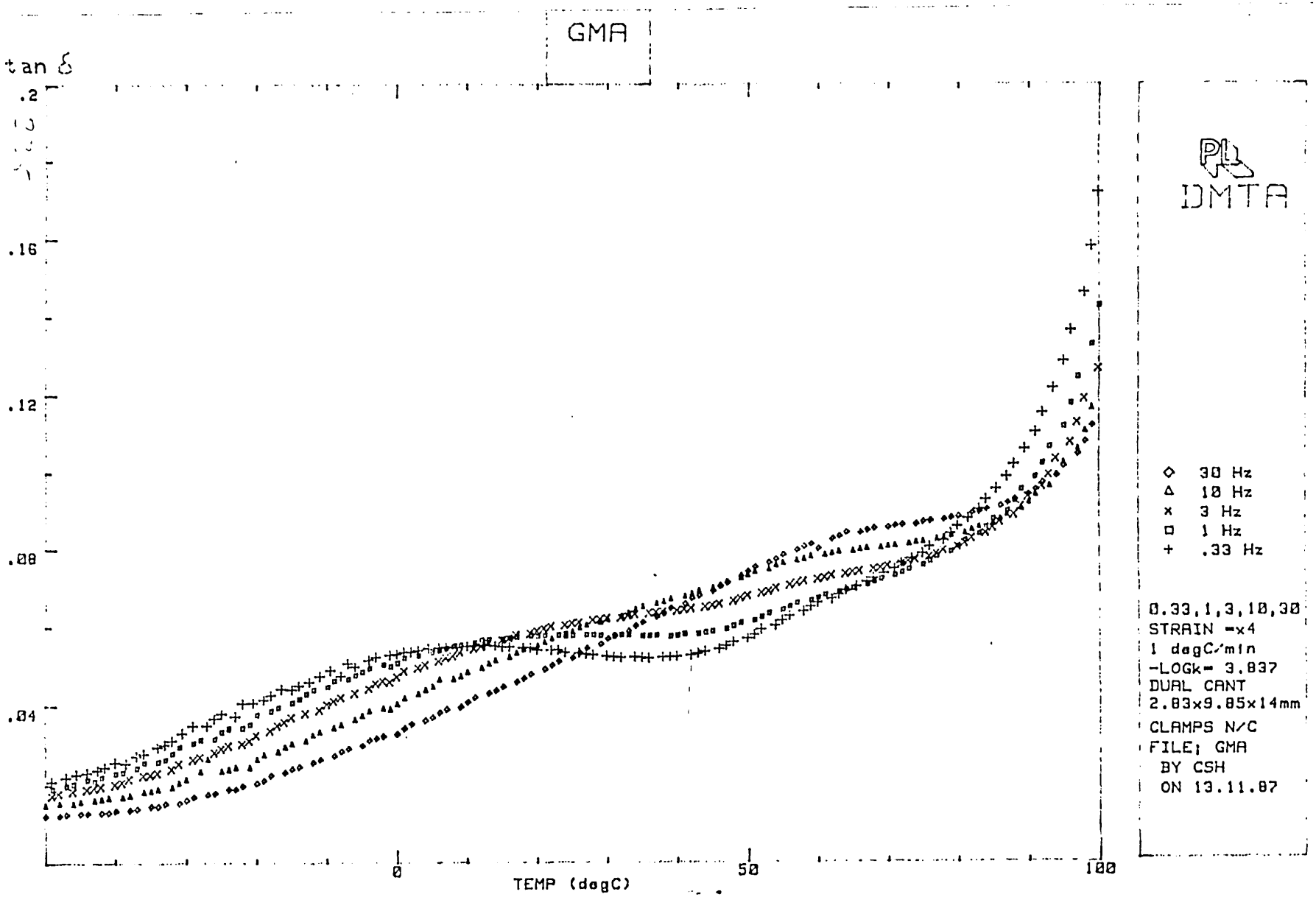


Figure 38 tan δ V's Temperature for BisGMA resin

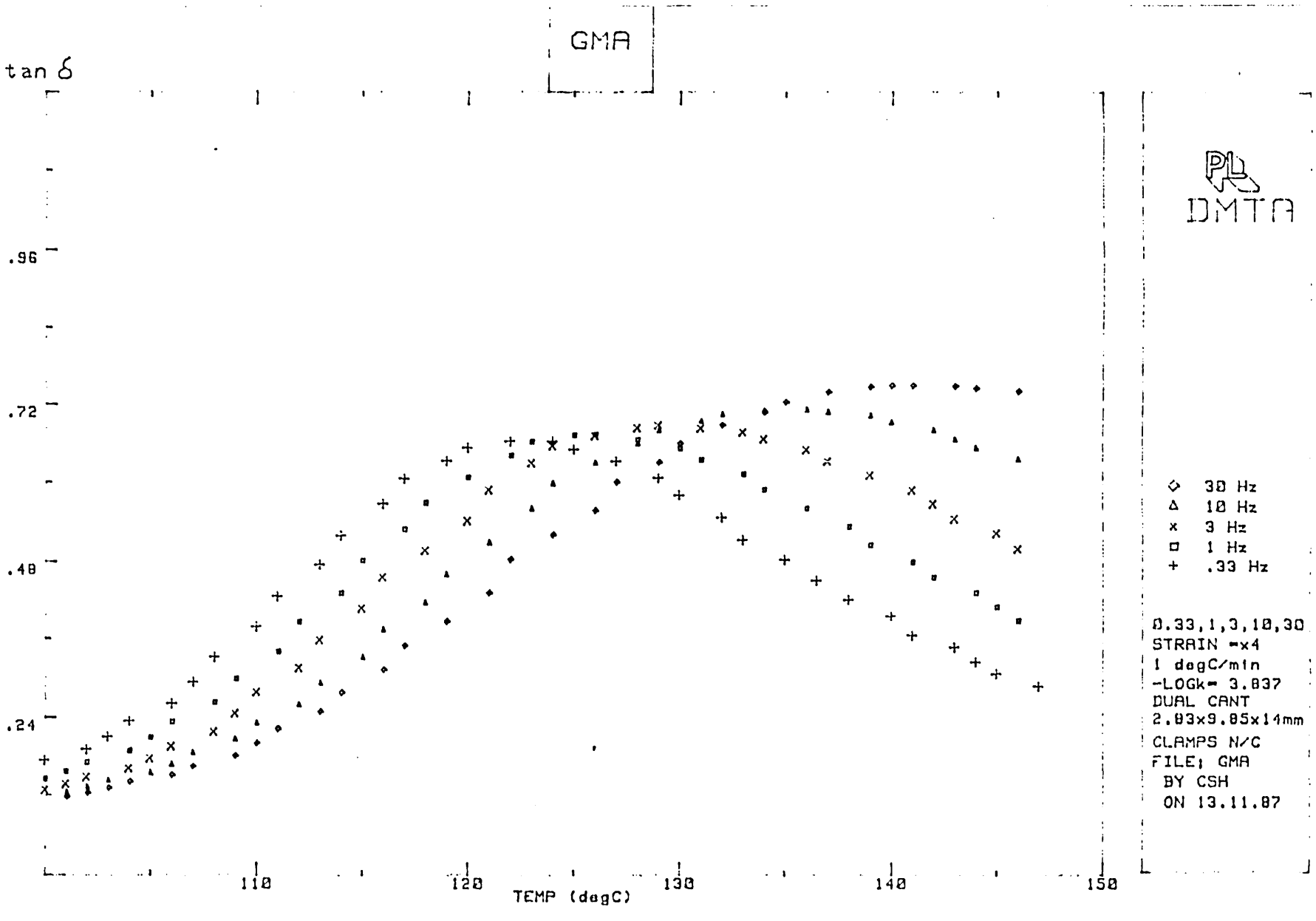


Figure 39 tan δ V"s Temperature for BisGMA resin

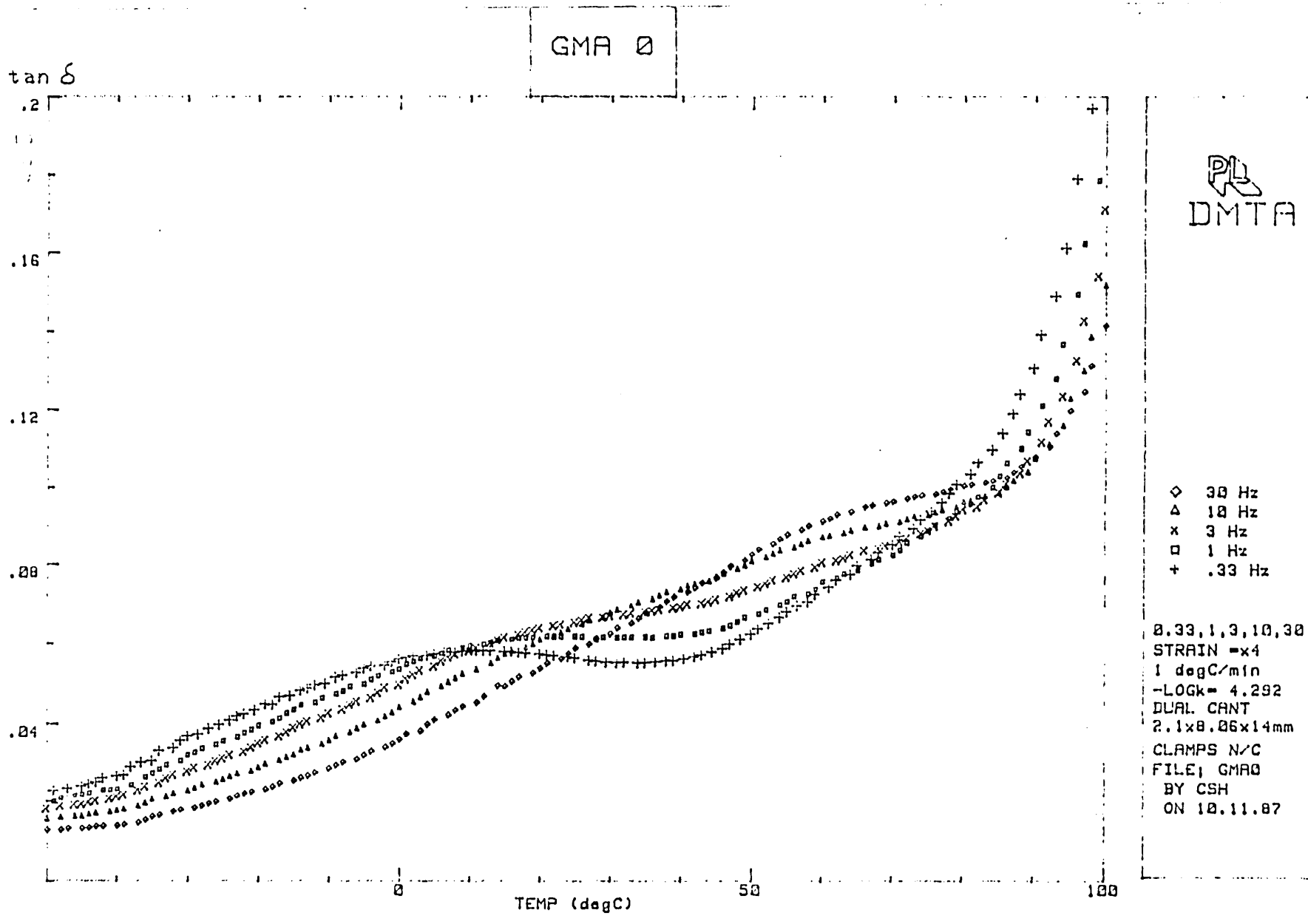


Figure 40 tan δ V's Temperature for BisGMAO resin

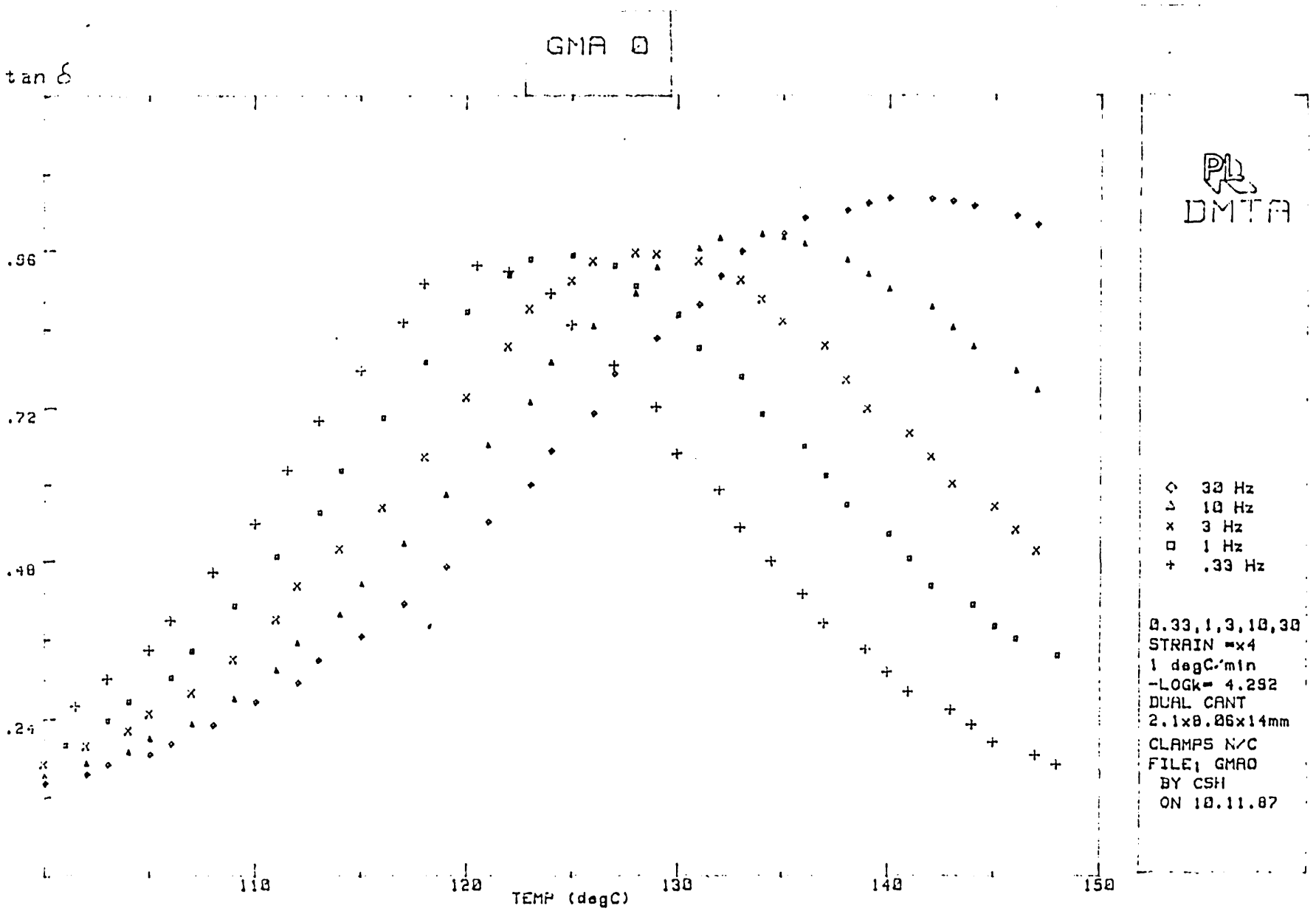


Figure 41 tan δ V's Temperature for BisGMAO resin

Results

(a) Flexural strength

	Mean ($\bar{X}$)	Standard Deviation
Bis GMAO material	143 MNm^{2}	6.76
BisGMA material	138 MNm^{2}	9.59

Statistical analysis of the results showed there was no significant difference between the flexural strength of the BisGMAO and BisGMA materials ($p \leqq 0.05$).

(b) Young's Modulus

	Mean ($\bar{X}$)	Standard Deviation
BisGMAO material	2.09	0.154
BisGMA	2.18	0.143

Statistical analysis: No significant difference between moduli of BisGMA material and BisGMAO ($p \leqq 0.05$)

(c) Viscous properties

Viscoelastic property	Tg	tanδ at Tg	E'158	$tan\delta_{37}$	Tg
BisGMAO material	125 C	0.9527	2.8 GPa	0.062	24 °C
BisGMA material	126 C	0.6729	5.2 GPa	0.058	23 °C

(d) Surface hardness

	Mean ($\bar{X}$)	Standard deviation
BisGMAO material	87	0.707
BisGMA material	87	0.632

Statistical analysis showed there to be no significant difference in surface hardness ($p \leqq 0.05$)

7.4 CONCLUSIONS

1. Several oxidising agents were used to convert the alcohol functional groups in BisGMA to ketones. The yields of these reactions were far lower than expected. This was attributed to the reaction conditions, eg temperature and pH, inducing polymerisation and/or decomposition of the BisGMA, thus reducing the yield.
2. The mechanical properties of two material formulations, one containing BisGMA, the other BisGMAO, did not significantly differ in the glassy state. In the rubbery state the BisGMA material was more rigid. This may be because the BisGMAO had oligomerised during synthesis. This would reduce the number of potential dimethacrylate molecules in the system and thus afford a lower degree of crosslinking. Another possible reason for the observed rigidity with BisGMA and not in the BisGMAO is that the BisGMA will have a greater degree of intermolecular forces. Therefore the network in the rubbery stage will be tighter, ie more elastic.

REFERENCES

1. BRADEN, M., Oper. Dent., 3, 97-102, (1978).

2. PEYTON, F.A. and CRAIG, R.G., "Restorative Dental Materials", Fourth edition. The G.V. Moseby Company, St Louis, (1971).

3. SKINNER, E.W. and PHILLIPS, R.W., "Science of Dental Materials". Saunders, Philadelphia, (1960).

4. GLENN, J.F., Polym. Sci. Technol., 14, 317-35 (1981).

5. ELLIS, B.and FARIJ, S.A.A., J. Dent., 8, 102-108, (1980).

6. SMITH, D.C., J. Prosthetic. Dent., 12, 1066, (1962).

7. DIRKSEN, L.C., J.A.D.A., 44, 265, (1952).

8. BRAUER, G.M., J.A.D.A., 72, 1151-1158, (1966).

9. CASWELL, C.W. and NORLING, B.K.J., Prothestic Dent., 55, 701, (1986).

10. WHITMAN, D., McKINNEY, J., HINMAN, R., HESBY, R. and PELLEN, G., J. Dent. Res., 64, IADR No 1746, (1958).

11. BRAUER, G.M. and CHEN, T.M., J. Dent. Res., 61, 1439-1443, (1982).

12. BRADEN, M. and DAVEY, K.W.M., UK Patent Application No. 8,416,754, (1984).

13. Dentsply International. European Patent Application, 80300030.6, (1980).

14. SPERLING, L.H., "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, (1981).

15. McPHERSON, J.P., Personal communication.

16. British Standards Institute, BS3990:(1980) Specification for Acrylic Resin Teeth.

17. American Dental Association, Specification No 15 for Synthetic Resin Teeth, (1985).

18. International Standards Organisation, 3336, Dentistry-Synthetic Resin Teeth, (1977E).

19. FRADOS, J. ed. "Plastics Engineering Handbook", Van Nostrand Rheinhold, New York, (1976).

20. BLOCK, H. and HOLLIDAY, A.K., "Modern Physical Chemistry. An Introductory Text.", Butterworths, London, (1976).

21. NEILSEN, L.E., "Mechanical Properties of Polymers and Composites", Marcel Dekker, New York (1974).

22. SEYMOUR, R.B. and CARRAHER, C.E., "Structure-Property Relationships in Polymers.", Plenum, New York, (1984).

23. TURNER, S., "Mechanical Testing of Plastics", Second edition, Longman, New York, (1983).

24. SNOOKS, A.M. and HARRIS, M., Ind. Eng. Chem., 37, 478, (1945).

25. VINCENT, P.I., Polymer., 1, 425, (1960).

26. BERRY, J.P., J. Polym. Sci (Part A), 2, 4069, (1964).

27. BERRY, J.P., J. Polym. Sci. (Part A), 1, 1003, (1963).

28. FERRICANE, J.L., Dent. Mater., 1, 11 (1985).

29. VON FRAUNHOFER, J.A., Br. Dent. J., 130, 243, (1971).

30. WALLS, D.C. AMER, O.C. and COMBE, E.C., Dent Mater, 3 265 (1987).

31. RUYTER, I.E., Acta Odont Scand. 39, 27-32, (1981).

32. McCRUM, N.G., READ, B.E. and WILLIAMS, G., "Anelastic and Dielectric Effects in Polymer Solids", Wiley, New York, (1967).

33. FERRY, J.D., "Viscoelastic Properties of Polymers", Wiley, New York, (1980).

34. BRADEN, M., J. Polym. Sci. (Part A)., 2, 1061-1065, (1964).

35. BRADEN, M. and STAFFORD, G.D., J. Dent. Res., 47, 519-523, (1968).

36. WHITING, R. and JACOBSEN, P.H., J. Dent. Res., 59, 55-60 (1980)

37. MURAYAMA, T., "Dynamic Mechanical Analysis of Polymeric Materials in Materials Science Monographs vol 1", Elsevier, Netherlands, (1978).

38. AKLONIS, J.J. and MacKNIGHT, W.I., "Introduction to Polymer Viscoelasticity", Wiley, New York, (1980).

39. BILLMEYER, F.W., "Textbook of Polymer Science.", Wiley, New York, (1984).

40. LETHERSICH, W., British Journal of Applied Physics, 1, 294, (1950).

41. NIELSEN, L.E., Soc. Plas. Eng. J., 16, 525, (1960).

42. FERRICANE, J.L. and GREENER, E.H. J. Biomed. Mater. Res. 20, 121 - 131 (1986).

43. BRADEN, M. and BARSBY, J.M., J. Dent. Res., 60, 146-148, (1981).

44. KINE, B.B., "Methacrylic Polymers" in "Kirk-othmer Encyclopedia of Chemical Technology", Vol 15, Wiley, New York, (1979).

45. COMBE, E.C., "Notes on Dental Materials", Churchill-Livingston, Edinburgh, (1986).

46. REES, D.G., "Essential Statistics" Chapman and Hall, New York, (1985).

47. PEGGIE, R.W. Personal communication.

48. "Instrument Manual for the Controlled stress rheometer", Carimed Ltd, Dorking, (1986).

49. DOOLITTLE, A.K., "Mechanisms of Plasticisation" in Bruins, P.F., Ed. Plasticiser Technology, Vol. 1. Reinhold, New York (1965).

50. HAN, C.D., "Rheology in polymer processing", Academic Press, New York, (1976).

51. BRYDSON, J.A., "Plastic Materials", Iliffe, London, (1969).

52. RUDIN, A., "The Elements of Polymer Science", Academic Press, New York, (1982).

53. ATKINS, A.G. and MAI, W.Y., "Elastic and Plastic Fracture", Ellis Hardwood, Chichester, (1985).

54. RUYTER, I.E. and SVENDSEN, S.A., J. Prosthet. Dent., 43, 95-104, (1980).

55. BOWEN, R.L., US Pat. No. 3,066,112., (1962).

56. CAULCUTT, R., "Statistics in Research and Development." Chapman and Hall, New York, (1983).

57. ASO, C. J., Polym. Sci., 34, 475-486, (1959).

58. WOLLFF, E.M., J.Aust. Dent., 7, 439-444, (1962).

59. STROH, A.N., J. Mech. Phys. Solids., 8, 119, (1960).

60. COWIE, J.M.G., "Polymers:Chemistry and Physics of Modern Materials." Intertext, Aylesbury, (1973).

61. RUYTER, I.E. and GYOROBSI, P.P., Scand. J. Dent. Res., 84, 396-400, (1976).

62. RUYTER, I.E., and OYSAED, H.J., Biomed. Mater. Res., 16, 741-754, (1982).

63. CAUSTON, B.E., "The Physical and Chemical Properties of Some Polymeric Dental Materials.", PhD Thesis, London University, London, (1972).

64. FERRICANE, J.L., "The Correlation between the Physical Properties and Degree of Conversion in Unfilled BisGMA-Based Dental Resins." PhD Thesis, Northwestern University, Illinois, (1983).

65. BAILEY, R.T., NORTH, A.M. and PETHRICK, R.A., "Molecular Motion in High Polymers.", Oxford Univ. Press, Oxford, (1981).

66. BRADEN, M. and CAUSTON, B.E., "Fracture of Polymers in Dental Applications", in "Developments in Polymer Fracture", Ed., Andrews E.H., Applied Science, New York, (1979).

67. KOBLITZ, F.F., STEEN, S.D. and KULP, P.R., "Relationship of Morphology to Mechanical Properties of Rapidly Polymerising Acrylic Dispersion", in "Toughmass and Brittleness of Plastics." Eds., Dean, R.D., Crugnola, A.M. American Chemical Society, (1976).

68. COOK, W.D., "Polymerisation Defects in Composite Resins" in "Posterior Composite Resin Dental Restorative Materials", Eds. Smith, D.C. and Vanherle, G., Peter Szulc, Netherlands, (1985).

69. NETER, J. WASSERMAN, W. and WHITMORE, G.A., "Applied Statistics", Allyn and Bacon, Boston, (1982).

70. STOODLEY, K.D.C., LEWIS, T. and STAINTON, C.L.S., "Applied Statistical Techniques.", Ellis Horwood, Chichester, (1980).

71. SCHEFFE, H., "The Analysis of Variance", Wiley, New York, (1959).

72. RYAN, B.F., JOINER, B.L. and RYAN, T.A., "Minitab Handbook", Duxbury Press, Boston, (1985).

73. HALL, M. and LEWIS, F., "Introduction to Polymer" in "Polymer Engineering - PT 614", The Open University, The Open University Press, Milton Keynes, (1984).

74. STEVENSON, G., "Worked Examples in Mathematics for Scientists and Engineers", Longman, New York, (1985).

75. ABELL, A.K., CRENSHAW, M.A. and TURNER, D.T., "Limiting Hardness of Polymer/Ceramic Composites", in "Polymers Science", Vol 14, Eds., Geblein, G.G., Koblitz, F.F., Plenum Press, New York, (1981).

76. BOWEN, K.L., J.A.D.A., **69**, 481-485, (1964).

77. CROSS, M., DOUGLAS, W.H. and FIELDS, R.P., J. Dent. Res., **62**, 850-852, (1983).

78. DE GEE, A.J., TEN HARKEL, E.C. and DAVIDSON, C.L., J. Dent. Res., 63, 532, (1984).

79. FAN, P.L., POWERS, J.M. and CRAIG, R.G., J. Dent. Res., 58, 2116-2119, (1979).

80. PHILLIPS, R.W., ST GERMAIN, H., ROBERTS, T.A., SWARTZ, M.L., and MOORE, B.K. J. Dent. Res., 64, 155-160, (1985).

81. DRAUGHN, R.A. and HARRISON, A., J. Prosthet. Dent., 40, 220-224, (1978).

82. HIRASAWA, T., Tokyo Med. Dent. Univ. Res. Inst. Dent. Mat., 2, 629-643, (1965).

83. SODERHOLM, K.J., "Effects of Water on Particle Reinforced Composites for Dental Use." M Phil Thesis, University of Sussex, (1979).

84. SODERHOLM, K.J., Acta. Odontal. Scand., 40, 145-50, (1983).

85. LI, Y., SWARTZ, M.L., PHILLIPS, R.W., MOORE, B.K. and ROBERTS, T.A., J. Dent. Res., 64, 12,1396-1401, (1985).

86. PILLAR, R.M., SMITH, D.C. and MARIC, B. J.Dent. Res., 65, 1308-1314, (1986).

87. SMITH, D.C., "Posterior Composite Dental Restorative Materials: Material Development", in "Posterior Composite Resin Dental Restorative Materials." Eds., Smith, D.C., and Vanherle, G., Peter Szulc, Netherlands, (1985).

88. GLENN, J.F., "Composition and Properties of Unfilled and Composite Resin Restorative Materials" in "Biocompatibility of Dental Materials.", Eds., Smith, D.C. Williams, D.F. Boca Raton:CRC Press, (1982).

89. BOWEN, R.L., MENIS, D.L., SETZ, L.E. and JENNINGS, K.A., "Theory of Polymer Composites" in "Posterior Composite Resin Dental Restorative Materials", Eds., Smith, D.C. and Vanherle, G., Peter Szulc, Netherlands, (1985).

90. PLUEDDEMANN, E.P., "Silane Coupling Agents", Plenum Press, New York, (1982).

91. SHELDON, R.P., "Composite Polymeric Materials", Elsevier, New York, (1982).

92. BOWEN, R.L., J.A.D.A., 69, 481-495, (1964).

93. CRAIG, R.G., "Overview of Posterior Composite Resins for Use in Clinical Practice" in "Posterior Composite Resin Dental Restorative Materials", Eds., Smith, D.C. and Vanherle, G., Peter Szulc, Netherlands, (1985).

94. SODERHOLM, K.J. and CALVERT, P.D., J. Mater. Sci., 18, 2957-2962, (1983).

95. HALL, M. and LEWIS, P., "Polymer Processing" in "Polymer Engineering-PT 614", The Open University, The Open University Press, Milton Keynes, (1984).

96. FERRICANE, J.L., MOSER, J.B., and GREENER, E.H. J. Dent. Res., 60, 1678-1685, (1981).

97. WATTS, D.C., COOMBE, E.C. and GREENER, E.H., J. Oral. Rehab, 7, 475-480, (1980).

98. GOLDMAN, M., Biomed. Mater. Res., 19, 771-783, (1985).

99. LLOYD, C.H. and Adamson, M., Dent. Mater., 3, 225-231, (1987).

100. SPANONDAKIS, J. and Young, R.J., J. Mat Sci., 19, 473-486, (1984).

101. LEWIS, T.B. and NIELSEN, L.E., J. Appl. Polym. Sci., 14, 1449, (1970).

102. WU, W. J., Dent. Res., 62, IADR No 285, (1983).

103. ASMUSSEN, E., Scand. J. Dent. Res., 90, 484-489, (1982).

104. HARRISON, A. and DRAUGHN, R.A., J. Prosthet. Dent., 36, 395-398, (1976).

105. McLEAN, J.W., Br. Dent. J., 110, 375-380, (1961).

106. WILSON, G.S., DAVIES, E.H. and VON FRAUNHOFER, J.A., BR. DENT. J., 148, 37-40, (1980).

107. RUYTER, I.E. and OYSAED, H., Acta. Odontol. Scand., 40, 179 - 192, (1982).

108. NEILSEN, L.E., Trans. Soc. Rheol., 13, 141-166, (1969).

109. ISHAI, O. and BODNER, S.R., Trans. Soc. Rheol., 14, 257-273, (1970).

110. RUYTER, I.E. and OYSAED, H., Acta. Odontol. Scand., 40, 319-324 (1982).

111. BOPNA, M.S., MUELLER, H.J. and KNOEPPEL, R., J. Dent. Res., 64, 1179-1184, (1985).

112. ATSUTA, M., ABELL, A.K., TURNER, D.T., NAKABAYASHI, N. and TAKEYAMA, J. Biomed. Mat. Res., 16, 619-628, (1982).

113. MISRA. D.N., J. Dent Res., 64, 1405-1408, (1985).

114. SUGARMAN, G. and MONTE, S.J., "Ken-React Reference Manual-Titanate, Zirconate and Aluminate Coupling Agents", Kenrich Petrochemicals, Bayonne, (1987).

115. SODERHOLM, K.J., J. Dent Res., 60, 1867-1875, (1981).

116. SCHRADER, M.E. and BLOCK, A., J. Polym. Sci. (Part C), 34, 281-291, (1971).

117. WILLEY, J.D., "Amorphous Silica" in Kirk-othmer Encylopedia of Chemical Technology", Vol. 20, New York, (1979).

118. CHACKO, V.O. Polym. Eng. Sci., 22, 968-974, (1982).

119. BRADEN, M., CAUSTON, B.E. and CLARKE, R.I., J.Dent. Res., 55, 730-732, (1976).

120. ANTONUCCI, J., Polym. Sci. Technol., 357-371, (1981).

121. RUYTER, E.I. and SIOVIK, J.I., Acta. Odontol. Scand., 39, 133-146,(1981).

122. SCHMITT, W., PURRMAN, R., JOCHUM, P. and WOLF, D.Z., US Patent No. 3,923,740 (1975).

123. STOFFEY, D.G. and LEE, L.L., US Patent No. 3,755,420, (1973).

124. WALLER, D.E., US Patent No. 3,709,866, (1973).

125. SCHMITT, W., US Patent No. 4,131,729, (1978).

126. BOWEN, R.L., US Patent No. 3,539,526, (1970).

127. LENZ, R.W., "Organic Chemistry of Synthetic High Polymers.", Wiley, New York, (1967).

128. FIESER, L.F. and FIESER, M., "Reagents for Organic Synthesis". Vol. 1, Wiley, New York, (1976).

129. COREY, E.J. and SUGGS, J.W. Tetrahedron Letts., 31, 2647-2650, (1975).

130. MORRISON, R.T. and BOYD, R.N., "Organic Chemistry", Allyn and Bacon, Boston, (1974).

131. DJERASSI, C., "The Oppeneaur Oxidation" in "Organic Reactions" Vol. 6, 207, (1951).

132. OPPENAUER, R.V., Org. Syn. Coll. Vol. 3, 207, (1955).

133. EASTHAM, J.F. and TERANISHI, R., Org. Syn. Coll. Vol. 4, 192, (1963).

134. OMURA, K. and SWERN, D. Tetrahedron., 34, 1651-1660, (1978).

135. SWERN, D., BROWNFAIN, D.S. and MANCUSO, A.J., J. Org. Chem., 44, 4148, (1979).

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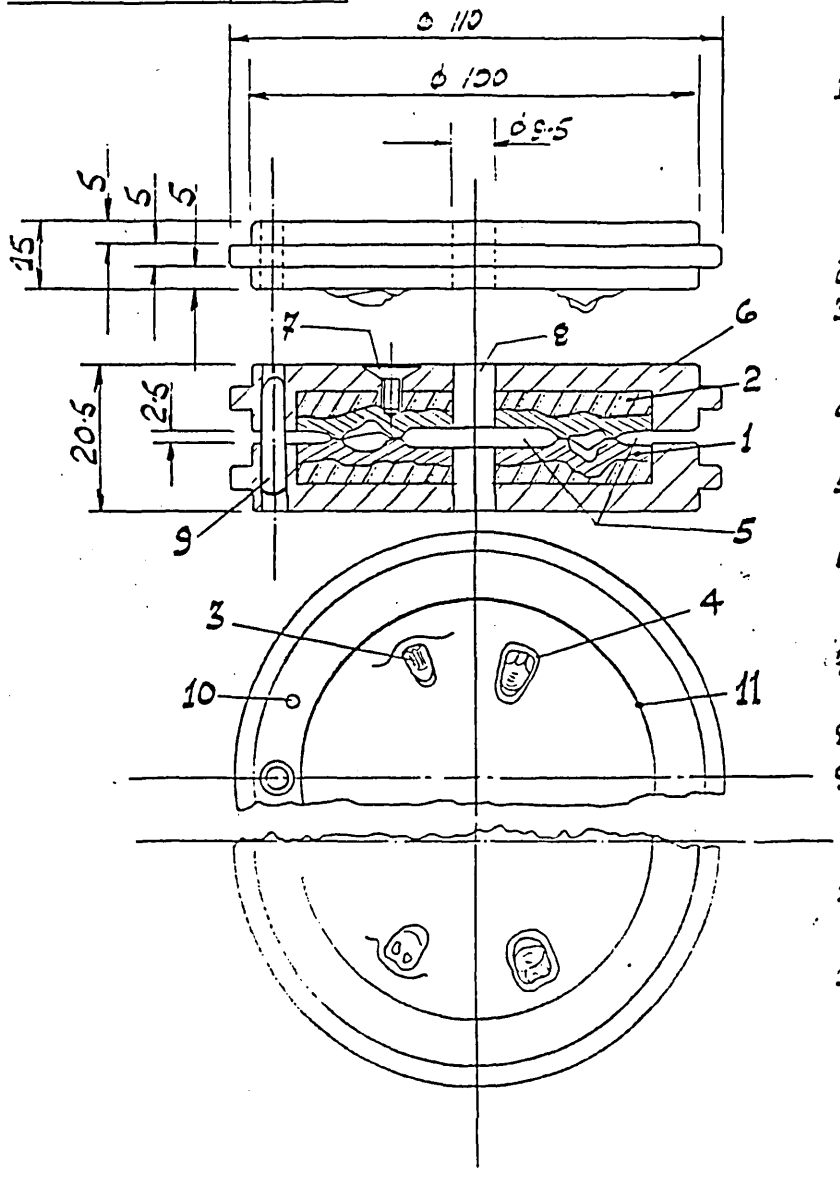


DO NOT SCALE

1. Electroformed Nickel To Rockwell 'C' 46-48 With A Minimum Thickness of 2mm.
   16 Cavity Posterior
   18 Cavity Upper Anterior
   29 Cavity Lower Anterior
2. Electroformed Copper To Rockwell 'B' 77
3. Blender or 3rd Part made Positive or Negative To Form Incisal As A First or Second Operation
4. Land Area of 1-2mm Around Cavity of Face and Back To Ensure Thin Flash
5. Adequate Relief To Aid Quick Dissipation of Heterial
6. Stainless Steel Frames To B.S EN58B AISI 321. Accurately Made For Use In Automatic Mould Openers or Hand Opening
7. Shell Held Firmly in Place With 3- Stainless Steel Screws.
8. Centre Hole Plugged With Hard Brass.
9. 3- Hardened And Precision Ground Taper Pins Ensure Accurate Cavity Alignment
10. 1. Hardened And Precision Ground Non Interchangeability Pin.
11. Shell Coaster Rotation Pin.

JOB No.	No. OFF	DATE	COMPANY

PART No.	No. OFF	MATERIAL	REMARKS

[redacted]

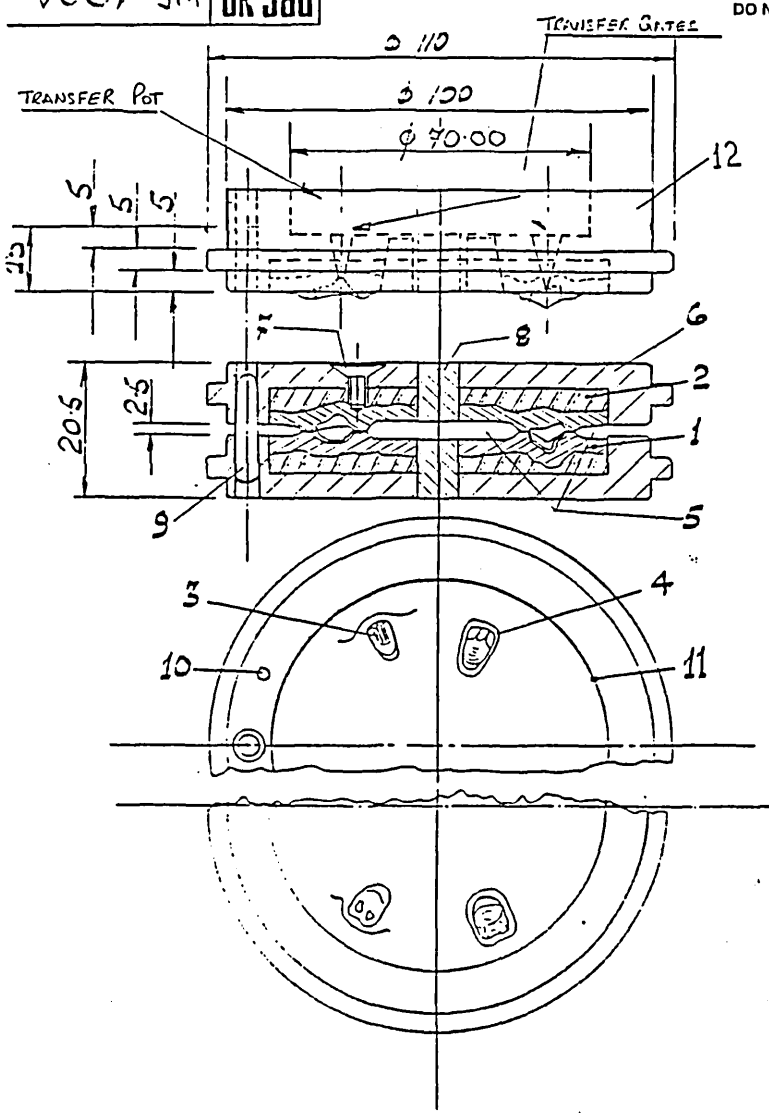
TITLE: Pictorial Detail of 2 and 3 Part Compression Mould.

Post
U. Ant
L. Ant

DIMENSIONS ON THIS DRAWING ARE	M.M.	DRAWN BY	[redacted] DATE 17/1/75
SCALE 1 : 1	TOLERANCES UNLESS STATED	CHECKED BY	DATE
PROJECTION	FRACTIONAL DIMENSIONS ± 1/64 DECIMAL DIMENSIONS ± .005" ANGULAR DIMENSIONS ± 1° METRIC DIMENSIONS ± .13mm	APPROVED BY	DATE
		JOB No.	DRG NO. WD 100

DRG NO. WD 1004

DO NOT SCALE



1. ELECTROFORMED NICKEL TO ROCKWELL 'C' 46-48 WITH A MINIMUM THICKNESS OF 2MM
   16 CAVITY POSTERIOR
   18 CAVITY UPPER ANTERIOR
   24 CAVITY LOWER ANTERIOR
2. ELECTROFORMED COPPER TO ROCKWELL 'E' 77
3. BLENDER OR 3RD PART MADE POSITIVE OR NEGITIVE TO FORM INCISAL AS A FIRST OR SECOND OPERATION
4. LAND AREA OF 1-2MM AROUND CAVITY OF FACE AND BACK TO ENSURE THIN FLASH
5. ADEQUATE RELIEF TO AID QUICK DISSIPATION OF METERIAL
6. STAINLESS STEEL FRAMES TO B.S EN58B AISI 321. ACCURATELY MADE FOR USE IN AUTOMATIC MOULD OPENERS OR HAND OPENING
7. SHELL HELD FIRMLY IN PLACE WITH 5- STAINLESS STEEL SCREWS.
8. CENTRE HOLE PLUGED WITH HARD BRASS.
9. 3 - HARDENED AND PRECISION GROUND TAPER PINS ENSURE ACCURATE CAVITY ALIGNMENT
10. 1 - HARDENED AND PRECISION GROUND NON INTERCHANGEABILITY PIN.
11. SHELL LOCATER ROTATION PIN.
12. TRANSFER MOULD BACK PART

JOB No.	No. OFF	DATE	COMPANY

PART No.	No. OFF	MATERIAL	REMARKS

[redacted]

TITLE: PICTORIAL DETAIL OF 2 AND 3 PART TRANSFER MOULD

U. ANT
L. ANT

DIMENSIONS ON THIS DRAWING ARE	MM.		
SCALE 1 = 1	TOLERANCES UNLESS STATED	DRAWN BY [redacted]	DATE 17/1/17
PROJECTION	FRACTIONAL DIMENSIONS ± 1/64	CHECKED BY	DATE
	DECIMAL DIMENSIONS ± .005"	APPROVED BY	DATE
	ANGULAR DIMENSIONS ± 1°	JOB No.	DRG NO. WD 1004
	METRIC DIMENSIONS ± 0.13mm		

The full text of the standard BS3990 : 1980 - Specifications for acrylic resin teeth - by the British Standards Institution (BSI), has been removed from the e-thesis due to copyright restrictions

Appendix 4

Hypothesis Testing

A hypothesis is a statement regarding the value of a population parameter. Sample data is used to validate the hypothesis. For example, the hypothesis "The hardness of a polymer is not effected by the level of initiator during the bulk polymerisation of the monomer" is tested for validity by comparison of the means of samples of monomers with different peroxide concentrations. For each sample the mean ($\bar{X}$), standard deviation (S) and variance (S^2) are calculated.

Before a test for difference in means it must be established that the population have the same variance

$$f_{test} \left(\frac{S_2}{S_1}\right)^2 \quad (32) \quad (S_2 > S_1)$$

The f_{test} value must be less than the f_{crit} value.

The critical value is found by referring to the f-distribution at the appropriate level of significance and degrees of freedom. The difference in means of two populations using unpaired data is calculated using the t-distribution.

$$t_{test} = \frac{\bar{X}_1 - \bar{X}_2}{S\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad (33)$$

$$\text{where } S = \sqrt{\frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}} \qquad (34)$$

This affords the observed t-value. If the difference between the two means μ_1 and μ_2 is significant at 5% level the value of t_{crit} must lie outside the t_{crit} value. The critical value is found by referring to the t-distribution tables at the appropriate level of significance and degree of freedom.

Appendix 5

Statistical Design of a quarter replicate of a 2^7 Factorial

The 128 combinations, or treatments, of the seven variables at two levels were determined.

In order to minimise chance effects, the treatments were listed in four columns of thirty two treatments. Each column was given a number from one to four. A coin was tossed twice to determine which thirty two treatments would be used as a head-head combination would correspond to column one, a heat-tail double toss would be number two, a tail head three, and a tail-tail equal to the fourth column. In doing this the choice of block was totally random.

Determination of Single Effects and Two Way Interactions

For each treatment a corresponding mechanical property was studied. In some cases, eg tensile strength, several measurements were made for each treatment. In such cases the mean, standard deviation, and, variance of these measurements were calculated. The values of the effects, and two-way interactions were determined as in equation (35) and (36).

$$\text{effect} = \frac{1}{16}\left[\left(\begin{array}{l}\text{sum of values which}\\ \text{have odd number of}\\ \text{variables}\end{array}\right) - \left(\begin{array}{l}\text{sum of values which}\\ \text{have even number of}\\ \text{variables}\end{array}\right)\right] \quad (35)$$

$$\begin{array}{l}\text{two-way}\\ \text{interaction}\end{array} = \frac{1}{16}\left[\left(\begin{array}{l}\text{sum of values which}\\ \text{have even number of}\\ \text{variables}\end{array}\right) - \left(\begin{array}{l}\text{sum of values which}\\ \text{have odd number of}\\ \text{variables}\end{array}\right)\right] \quad (36)$$

If the value of the effect or interaction is positive, then the variable or combination of variables will increase the mechanical property being studied. If the value is negative the variable or combinations of variables have a detrimental effect on the mechanical property.

Levels of Significance

After establishing the magnitude of an effect it must be determined if the effect or interaction is statistically significant.

Stating that any effect or interaction is statistically significant implies that the observed observations has not occurred by chance, but purely from the influence of the variable(s). Confidence limits for such a prediction are applied. In this work the confidence limits were 99% or 96%. That is to say, that any observed statistically significant effect or interaction was due to the particular variables 99 times out of 100. The other one time is due to chance. An effect or interaction is significant if its value is above an upper limit or below a lower limit. The limiting values are determined by applying equation (37). The greater the difference between the value of an effect and a limit, the greater the significance of the effect.

$$\text{Limiting value} = \pm\sqrt{\frac{4.F.\hat{\sigma}^2}{a.b.2^7}} \qquad (37)$$

where F = probability factor (f-distribution)

a = fraction of replicate

b = no of repeats of observation

$\hat{\sigma}^2$ = Average of variances

The variance is a measure of error in the experiment. The error may also be estimated by assuming that the 3 way, or greater, interactions are insignificant and are so small that they are considered to be error. The average value is therefore the sum of these interactions divided by their number.

Appendix 6

Two Way Analysis of Variance

An experiment is designed to show the effect of variables at different levels has on a dependent variable. However, how does the analyst know if the difference between levels is due to the factor or due to experimental error?

It may be shown that the total variation of an observation from the mean can be subdivided into three parts, one for each factor in the analysis and the third part is for the residual variation. This is the parametric model.

$$\text{Total Sum of Squares} = \left[\text{Factor A Sum of Squares (SSA)}\right] + \left[\text{Factor B Sum of Squares (SSB)} + \text{Residual Sum Squares (error), (SSE)}\right] \quad (38)$$

If there are h levels of factor A and g levels of B, then the estimate of the sum of squares of the error, E(SSE), is

$$E(SSE) = (h-1)(g-1)\sigma^2 \quad (39)$$

For a null hypothesis of no difference between the levels of A, there are two estimates for σ^2,

$$\hat{\sigma}_1^2 = {}^{SSE}/_{(h-1)(g-1)} \quad (46) \quad \text{and} \quad \hat{\sigma}_2^2 = {}^{SSA}/_{(h-1)} \quad (41)$$

Any difference between σ_1^2 and σ_2^2 is tested for utilizing the one sided F test (Appendix 4). If the difference between the two estimates is found to be significant then there is a difference between the levels of A and the null hypothesis is rejected. This is repeated for B.

If each treatment is repeated then any interaction effect between A and B may be tested for. Once again the sum of squares method is applied.

$$SST = SSA + SSB + SSI + SSE \quad (42)$$

where SSI = sum of squares due to interaction of A and B.

The interaction mean square is tested against the residual mean square, using a one sided F test.

The main effect mean squares of A and B are also tested against the residual mean square.

eg test statistic for the interaction effect of A and B is given by

$$F_{test} = \hat{\sigma}_4^2 / \hat{\sigma}_2^1 = \frac{SSI / [(h-1)(g-1)(N-hg)]}{SSE / (N-hg)} \quad (43)$$

where N = number of observations

If $F_{test} > F_{crit}$ then there is a significant effect due to the interaction of A and B.

Appendix 7

Scheffés S test

The two way ANOVA test highlights if there is a difference between levels of a factor, eg A. Scheffé S test tell the analyst at which level the difference occurs.

Scheffés S method allows the analysis of a contrast and gives confidence limits valid for all contrasts.

If $\phi = \Sigma C_i \beta_i$ then we reject that there is no difference in levels if:

$$\hat{\phi} > (I-1) F_{\alpha I-1,(h-1)(g-1)} \hat{\sigma}_\theta \qquad (44)$$

When ϕ = contrast

C_i = coefficients of β_i

β_i = theoretical population mean at level i

$F_{\alpha I-1,(h-1)(g-1)} = F_{critical}$

I = No of levels of the factor under consideration.

$\hat{\phi}$ = estimates of $\phi = \Sigma C_i \hat{\beta}_i$. (45)

$\hat{\beta}_i$ = estimates of $\beta_i = \Sigma Y_i / n_i$ (46)

$\hat{\sigma}_\theta$ = standard error of $\phi = \frac{\Sigma C_i^2 \sigma^2}{n}$ (47)

σ^2 = estimate of variance of residual error = $SSE / (n-1)(g-1)$ (48)

Appendix 8

Regression Analysis

When analysing the relationship between several independent variables and a particular dependent variable, (y), it may be of use to generate a model which will predict the value of y at given values of the independent variables. If only one independent variable is analysed the technique used is simple linear regression. If more than one independent variable is studied this is called multiple regression analysis.

For example, the model $y = \alpha + \beta x$ is tested by linear regression analysis. If this relationship does exist within the sample data, both the direction and the strength of the relationship, the goodness of fit, can be measured using the coefficient of determination, r^2,

$$r^2 = 1 - \frac{\Sigma(y-\hat{y})^2}{\Sigma(y-\bar{y})^2} \times 100 \qquad (49)$$

The numerator is a measure of how well the fitted values compare to the actual values. The denomenator is a measure of the variability of data. The greater the r^2 value the better the model fits the experimental values. In multiple regression analysis, rather than the model fitting a line or a curve it fits a plane - ie it is in 3 dimensions. However, r^2 is used to determine how well the model fits the data.

Stepwise regression is an automatic technique which inserts variables into an equation one at a time but removes a variable that has become redundant at any stage.

eg (1) $y = 4 \times 3x$ $\quad r^2 = 45\%$

(2) $y = 14 + 2.3x + x^2$ $\quad r^2 + 76\%$

(3) $y = 5.4 + 13x + x^2 + 4.1xz$ $\quad r^2 = 89\%$

(4) $y = 2.4 + x^2 + 8.1 \times 2 + z^2$ $\quad r^2 = 89.1\%$

(5) $y = 4.1 + 2x^2 + 3z^2$ $\quad r^2 = 88.4\%$

From (1) to (3), the analysis adds variables to the model. However, at (4) if z^2 is added and 13x removed, the fit is improved. Also if xz is removed from (4), the degree of fit is almost as good and it has the advantage of being a simpler model.

Appendix 9

Mann-Whitney-U-test

The Mann-Whitney-U-test is a procedure which tests two means that does not require the assumption of normal distributions. The test is an alternative to the t-test which do contain this assumption. The hypothesis for the Mann-Whitney tests are the same as for the t-tests.

$H_0: \mu_1 = \mu_2$

$H_a: \mu_1 \neq \mu_2$

The first step is to combine the two samples into a large sample, and then determine the rank of each observation in the large sample. The sum of the ranks of the first sample is T_1 and the sum of the ranks of the second T_2. H_0 is rejected if T_1 is significantly greater than T_2.

For small samples it is assumed:

1. Random samples are obtained from each population.
2. The two samples are independent.
3. The samples data are at least ordinal.

The procedure is:

1. $n_1 \leq n_2$
2. Determine U_1 and U_2 using equations (50) and (51).
3. Use the distribution function for the Man-Whitney U statistic to test H_0 versus H_a, where small values of p lead to the rejection of H_0. (Generally if the p-value is ≤ 0.05, then reject H_0).

$$U_1 = n_1 n_2 + \frac{n_1(n_1 + 1)}{2} - T_1 \qquad (50)$$

$$U_2 = n_1 n_2 + \frac{n_2(n_2 + 1)}{2} - T_2 \qquad (51)$$